A Single-Crystal Neutron Diffraction Study of Heavy Ice*

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Neutron diffraction measurements of the $h0l$ reflections of crystalline D_2O at $-50°$ C. and $-150°$ C. are consistent with the disordered model of Pauling. The O–D distances are both $1·01$ Å and the D–O–D angles are close to tetrahedral. Analysis of the thermal parameters resulting from a complete least-squares refinement of the structure clearly demonstrates anisotropy of deuterium motion, and yields values for the amplitude of the O–D stretching vibration consistent with the frequency of this motion.

Introduction

While the symmetry, unit cell, and oxygen-atom arrangement of ice were determined in an X-ray study by Barnes (1929), the hydrogen-atom arrangement has eluded an experimental determination and has drawn a great deal of theoretical interest. A detailed review of work to 1951 has been prepared by Owston (1951). The most important evidence concerning the hydrogen arrangement is doubtless the residual entropy found by Giauque & Ashley (1933) and its interpretation in terms of structural disorder by Pauling (1935). In Pauling's model, one hydrogen atom is assumed to lie on each line connecting adjacent oxygen atoms, closer to one oxygen atom than to the other. Only two hydrogen atoms are situated close to any one oxygen. All configurations compatible with these restrictions are assumed equally probable. The resulting structure conforms statistically to the symmetry and unit cell described by Barnes (1929) and the 'average' structure, which determines the Bragg diffraction pattern, may be specified by assigning a half-hydrogen atom to each of the 4N sites contained within an array of N oxygen atoms. The neutron diffraction study of Wollan, Davidson & Shull (1949) gave results consistent with this 'half-hydrogen' description, and discriminated against several alternative models.

Two studies have recently caused reconsideration of the correctness of this model. Measurements by Rossmann (1950) appeared to indicate that ice crystals, when 'untwinned', are piezoelectric. Approximate calculations by Bjerrum (1952) of the mutual electrostatic energy of the several arrangements of neighboring water molecules in ice indicated differences in energy sufficient to make untenable Pauling's assumption of equal probability. Stimulated by these studies, Rundle (1953) has suggested a polar model of ice which would provide residual entropy, though not quantitatively that observed (Lipscomb, 1954; Rundle,

1954). Owston (1953) has devised structures of monoclinic symmetry which conform to Bjerrum's stable arrangements.

Piezoelectricity in ice has remained unconfirmed and now appears to have been erroneous (Mason & Owston, 1952; Steinemann, 1953). Very recently, Pitzer & Polissar† (1956) re-examined Bjerrum's calculation and were able to demonstrate that his conclusions are largely negated when certain additional interactions neglected by Bjerrum are included.

The chief structural evidence available for a test of the various proposals has been the neutron diffraction data of Wollan *et al.* (1949) but these data, because they are derived from powder measurements of poor resolution, have proved to be quite inadequate for the purpose. The single-crystal neutron diffraction method has been shown (Peterson & Levy, 1951) to be capable of providing a greater abundance of data with excellent resolution, and in addition makes possible application of improved methods of refinement. This paper reports on the application of the single-crystal method to the problem of the ice structure. The results support the half-hydrogen description of the ice structure and thus are consistent with the Pauling model.

Unit cell and space group

X-ray studies (Barnes, 1929) assigned ice to the hexagonal space group D_{6h}^4–$C6/mmc$. Oxygen atoms were placed in the fourfold positions (f) (*International Tables*, 1952):

$$\pm(\tfrac{1}{3}, \tfrac{2}{3}, z; \tfrac{2}{3}, \tfrac{1}{3}, \tfrac{1}{2}+z)$$ with z assigned a value of $\tfrac{1}{16}$.

Hydrogen or deuterium atoms are assigned, in the Pauling model, 4 half atoms to positions (f) and 12 half atoms to the 12-fold two-parameter positions (k):

$$\pm(x, 2x, z; \ x, \bar{x}, z; \ 2\bar{x}, \bar{x}, z; \ x, 2x, \tfrac{1}{2}-z;$$
$$x, \bar{x}, \tfrac{1}{2}-z; \ 2\bar{x}, \bar{x}, \tfrac{1}{2}-z).$$

The oxygen atoms and the deuterium atoms in positions (*f*), henceforward designated D_1, lie on three-fold axes. The remaining deuterium atoms, designated D_2, lie in mirror planes.

In the Rundle polar model of ice the space group is C_{6v}^4, which gives the same extinctions as D_{6h}^4. In this model oxygen atoms are assigned to two sets of two-fold positions (*b*). The ordered hydrogen atoms are assigned to another set (*b*) and the disordered hydrogens are assigned to two sets of 6-fold positions (*c*) with $\frac{1}{3}$ hydrogen to each and to a set of 12-fold positions (*d*) with $\frac{1}{6}$ hydrogen to each.

Axial lengths were interpolated from those reported by Megaw (1934) and Vegard & Hillesund (1942) to yield the following values at the temperatures of these studies*:

	a	*c*
− 50° C.	4·513 Å	7·355 Å
−150° C.	4·489	7·327

Experimental

Heavy-ice crystals were grown in test tubes placed in an insulating block in a cold chest. The frozen cylinders were examined in polarized light, and single-crystal portions were located. A single-crystal section of an appropriate size was mounted on a goniometer head and examined in a neutron beam while chilled in a stream of cold nitrogen gas after the method of Post, Schwartz & Fankuchen (1951). The specimen was oriented with an [01.0] axis vertical and shaped approximately to a cylinder, about 4 mm. in diameter by 12 mm. high, with the cylinder and zone axes coinciding. Complete [01.0] zone data were then collected out to $\sin\theta/\lambda = 0.75$ with $\lambda = 1.062$ Å. Measurements were made at temperatures of −50° C. and −150° C.; the temperature was recorded throughout, and the extreme variation was less than ±5° C. Data collection was carried out in a fashion previously described (Peterson & Levy, 1952), except that reorientation of the crystal for the various reflections was automatically accomplished by use of a crystal rotator and associated timing circuits which have been developed in this laboratory. Data collection took place over a period of about one week at each temperature. Several reflections were checked at the beginning and end of the measurement to insure that the diffracted intensities were constant within experimental error over this period.

The hexagonal symmetry of ice was confirmed in preliminary measurements by checking the equality of neutron intensity of equivalent reflections of the type (*hk*.0) related by 60° rotations, using a specimen with [00.1] zone axis vertical. The space-group absences of D_{6h}^4 were checked and found to be absences for neutron diffraction also. Some exploration was

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* Since the reported values appear to be somewhat non-concordant, the interpolated values are considered significant only to about 0·005 Å.

made for possible superlattice reflections but none was found. Thus ordered asymmetrical structures of the type suggested by Owston (1953) associated with an enlarged unit cell of lower than hexagonal symmetry are rendered improbable.

Preliminary treatment of data

−50° C. *data*

Observed structure factors were derived from measured integrated intensities in the usual way, and a preliminary scale of absolute intensities was established by normalization to the average of (100) and (101), which are quite insensitive to the model assumed. Comparison of this set of experimental structure factors with those calculated for half-hydrogen and Rundle-type models (using an assumed O–H distance of 0·96 Å) was made, and it was at once apparent that the Rundle model was not tenable whereas the half-hydrogen model showed promise of successful refinement. Table 1 shows this comparison for the reflections

Table 1. *Comparison of observed structure factors with those computed for Pauling and Rundle models*

h0l	Pauling model	Rundle model	Exp. (−50° C.)
103	−1·47	−2·14	1·59
203	1·02	1·38	1·08
301	−0·22	0·77	0·22
302	−0·65	0·91	0·65
303	−0·59	0·97	0·60
305	−0·77	1·08	0·72
404	0·01	0·30	0·12
405	−0·55	0·68	0·59
109	0·25	0·32	0·24
0,0,10	0·22	0·37	0·28
505	0·21	0·41	0·18

which are especially sensitive to model differences. There was little evidence of extinction even for the most intense reflections, as evidenced by the agreement between calculated and experimental structure factors. The Fourier method was then applied; the assignment of signs of the experimental structure factors was made on the basis of the Pauling model. No modification function was used since the Fourier series appeared to be fairly well converged. Position parameters and temperature factors were obtained by analysis of the experimental map and used in a new structure-factor calculation. The agreement factor $\Sigma||F_o|-|F_c||\div\Sigma|F_o|$ at this stage was approximately 13%. Several sign changes occurred and a new experimental Fourier map was prepared as well as a calculated map for back-shift purposes. The back-shifted parameters resulting from this stage of the analysis led to an agreement factor of 10%, omitting several weak terms whose signs were still undetermined.

Several other Fourier syntheses, including a difference synthesis in which oxygen atoms were removed, were made in an attempt to refine the para-

meters further but the overall result was an agreement factor of 9·5%. A representation of the final Fourier map is shown in Fig. 1. Then trial variations of scale factor, deuterium scattering factor and individual atom temperature factors were carried out systematically,

Fig. 1. Fourier projection along **b** of the scattering density in D_2O ice at $-50°$ C. The numerical values are the maxima of the density function in Fermi units (10^{-12} cm.) per Å^2. The abscissa is $a \sin 120°$. The contour interval is 0·25, zero contour omitted. The extreme variation of density in the background region is $+0·16$ to $-0·15$.

leading to an improved agreement factor of 6·3% in which unobserved reflections were included at half the minimum observable value. Attempts to improve the agreement at this stage by allowing for asymmetry in temperature motion were unsuccessful.
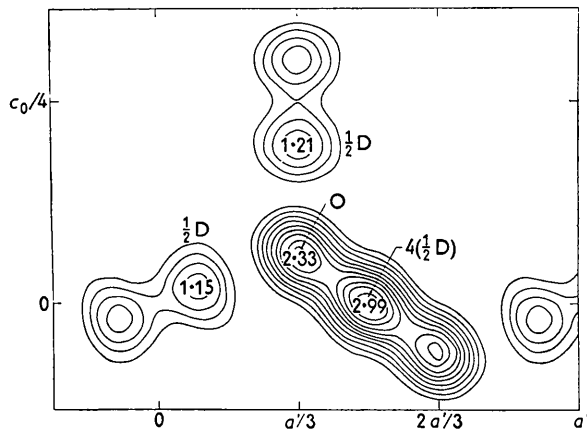
$-150°$ C. *data*

The possibility still remained that ordering of the ice structure might occur at lower temperatures, especially in view of the considerable changes in physical properties that are known to occur below $-50°$ C. Hence a second heavy-ice specimen was prepared, shaped and oriented, and an entirely independent set of intensities was measured at a temperature of $-150°$ C. This specimen was also investigated for hexagonal symmetry and forbidden reflections and no anomalies were noted. The strongest reflections, notably (100), (002), (101) and (004), showed evidence of extinction when measured on this specimen. The intensities were approximately normalized and experimental structure factors were determined. Direct comparison of these with calculated structure factors based on Pauling and Rundle models again definitely eliminated the latter model and showed excellent agreement with the former one. The agreement factor was low (approximately 8%) from

Table 2. *Symmetry relations between thermal parameters of positions (f) and (k) of space group $D_{6h}^4 - C6/mmc$*

Positions*	h^2	k^2	l^2	hk	kl	lh
(f) $\frac{1}{3}, \frac{2}{3}, z$	β_{11}	β_{11}	β_{33}	β_{11}	0	0
$\frac{1}{3}, \frac{2}{3}, \frac{1}{4}-z$	β_{11}	β_{11}	β_{33}	β_{11}	0	0
(k) $x, 2x, z$	β_{11}	β_{22}	β_{33}	β_{22}	β_{31}	$\frac{1}{2}\beta_{31}$
$2\bar{x}, \bar{x}, z$	β_{22}	β_{11}	β_{33}	β_{22}	$-\frac{1}{2}\beta_{31}$	$-\beta_{31}$
$x, \bar{x}, z$	β_{11}	β_{11}	β_{33}	$2\beta_{11}-\beta_{22}$	$-\frac{1}{2}\beta_{31}$	$\frac{1}{2}\beta_{31}$
$x, 2x, \frac{1}{4}-z$	β_{11}	β_{22}	β_{33}	β_{22}	$-\beta_{31}$	$-\frac{1}{2}\beta_{31}$
$2\bar{x}, \bar{x}, \frac{1}{4}-z$	β_{22}	β_{11}	β_{33}	β_{22}	$\frac{1}{2}\beta_{31}$	β_{31}
$x, \bar{x}, \frac{1}{4}-z$	β_{11}	β_{11}	β_{33}	$2\beta_{11}-\beta_{22}$	$\frac{1}{2}\beta_{31}$	$-\frac{1}{2}\beta_{31}$

* Positions related to those listed by a center of symmetry have the same coefficients.

Table 3. *Parameters of the structure of ice and their standard errors*

	$-50°$ C.		$-150°$ C.	
	Preliminary refinement	Least-squares output	Preliminary refinement	Least-squares output
Scale factor	1·000	0·975 ±0·031	1·000	1·005 ±0·021
f_D	0·656	0·672 ±0·025	0·656	0·650 ±0·014
z_O	0·0625	0·0629±0·0006	0·0625	0·0620±0·0004
z_{D_1}	0·200	0·1989±0·0009	0·200	0·1980±0·0007
x_{D_2}	0·455	0·4551±0·0013	0·455	0·4545±0·0009
z_{D_2}	0·0175	0·0182±0·0006	0·0175	0·0172±0·0004
$4\beta_{11}(O)/b_1^2$	2·30	2·39 ±0·22	1·50	1·53 ±0·11
$4\beta_{33}(O)/b_3^2$	2·30	2·29 ±0·17	1·50	1·48 ±0·10
$4\beta_{11}(D_1)/b_1^2$	2·90	3·23 ±0·22	2·40	2·41 ±0·13
$4\beta_{33}(D_1)/b_3^2$	2·90	2·97 ±0·28	2·40	1·81 ±0·12
$4\beta_{11}(D_2)/b_1^2$	2·90	3·30 ±0·27	2·40	2·29 ±0·21
$4\beta_{22}(D_2)/b_1^2$	2·90	2·80 ±0·26	2·40	1·85 ±0·12
$4\beta_{33}(D_2)/b_3^2$	2·90	3·05 ±0·15	2·40	2·43 ±0·10
$4\beta_{31}(D_2)/b_3 b_1$	0	0·48 ±0·37	0	0·48 ±0·18

the start and the position parameters required no revision from those at the higher temperature. Trial variations of temperature factors and scale factor were made which led to an agreement factor of 6·9% omitting extinction-affected reflections.

Least-squares refinement

Parameters obtained from both sets of data were subsequently refined further by a complete least-squares treatment, varying all independent position and temperature factor parameters. The analysis was carried out on a high-speed electronic computer, the Oracle, making use of a code developed by W. R. Busing and H. A. Levy (unpublished work). General asymmetric temperature factors of the form

$$\exp\ -[(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{23}kl+\beta_{31}lh)]\quad(1)$$

were assumed. For the positions occupied in ice, the coefficients β are constrained by symmetry (Levy, 1956), so that there are two independent coefficients for O and D_1 and four for D_2. These relationships are listed in Table 2. It is apparent from the table that all the independent β's are determinable from $h0l$ measurements alone.

The function $R = \Sigma w(hkl)(F_o(hkl)-F_c(hkl))^2$ was minimized; off-diagonal terms in the normal equations were included. The input data were weighted according to the following scheme. The variance of an integrated intensity measurement was taken to be equal to the total count in a peak, plus twice the background count, plus the quantity $(0\cdot02E)^2$. The latter quantity, which represents a contribution of 2% of the integrated intensity E to the standard deviation of E, was intended to allow for inconstancy of the primary beam, errors in absorption correction, and the like. The expression for the weight of a measurement was then

$$w_{hkl}^{-1} = \frac{1}{4}\frac{F^2}{E^2}\left[\frac{1}{n}(E+2B)+(0\cdot02E)^2\right],$$

where n is the number of repetitions of the measurement.

For both sets of data, unobserved reflections were entered at one-half the minimum observable value. In the case of the $-150°$ C. data, an extinction correction was applied to the observed structure factors. For this purpose it was assumed that the effective absorption coefficient was $\mu+gE$, and the constant g was chosen to give satisfactory agreement with calculation for (101) and (004). Only four reflections (see Table 4) were appreciably affected. In weighting the observations for the least-squares refinement, a term equal to the square of 20% of the extinction correction was added to the variance of E.

The weighted least-squares analyses were carried out for three cycles with 56 observations and the 14 parameters listed in Table 3. Changes on the final cycle were negligible. Following the final cycle, the matrices

Table 4. *Structure factors for* D_2O *ice at* $-50°$ C. *and* $-150°$ C.

$h0l$	$-50°$ C.		$-150°$ C.	
	$F_{calc.}$	$F_{exp.}$*	$F_{calc.}$	$F_{exp.}$*
100	−3·11	2·87	−3·10	2·64†
002	4·26	3·99	4·25	4·57†
101	−1·92	1·99	−1·90	1·91†
102	−1·52	1·61	−1·56	1·50
103	−1·47	1·55	−1·52	1·55
200	0·77	0·88	0·75	0·81
201	1·55	1·60	1·60	1·48
004	3·17	3·14	3·28	3·31†
202	1·86	1·79	1·90	1·74
104	−1·11	1·20	−1·17	1·16
203	1·01	1·05	1·12	1·18
105	−1·84	1·83	−1·99	1·96
204	1·52	1·52	1·63	1·56
300	1·26	1·25	1·41	1·46
301	−0·23	0·21	−0·25	0·28
302	−0·64	0·63	−0·68	0·72
006	1·02	0·98	1·17	1·15
205	1·23	1·24	1·43	1·45
106	−0·23	0·29	−0·28	0·34
303	−0·61	0·59	−0·67	0·63
304	−0·69	0·68	−0·80	0·78
206	1·42	1·39	1·63	1·62
107	−1·25	1·16	−1·56	1·54
400	−0·83	0·88	−1·06	1·04
305	−0·79	0·70	−0·91	0·91
401	−0·83	0·83	−1·01	1·02
402	−0·14	0·17	−0·22	0·28
207	0·72	0·73	0·99	0·95
008	−0·64	0·65	−0·93	0·92
403	−0·53	0·52	−0·69	0·72
108	0·45	0·48	0·62	0·60
306	−1·19	1·14	−1·47	1·47
404	0·03	< 0·12	0·07	0·15
208	1·23	1·29	1·66	1·65
307	−0·75	0·82	−0·93	0·91
405	−0·58	0·58	−0·80	0·81
109	0·24	0·23	0·49	0·46
500	−1·13	1·11	−1·59	1·55
501	0·48	0·53	0·66	0·64
502	−0·63	0·62	−0·92	0·86
406	0·24	0·22	0·31	0·33
209	−0·56	0·53	−0·80	0·81
308	−1·42	1·43	−2·09	2·01
503	0·22	0·18	0·35	0·31
0,0,10	0·20	0·27	0·29	0·30
1,0,10	−0·04	< 0·12	0·06	< 0·12
504	−0·40	0·19	−0·61	0·61
407	−0·23	0·23	−0·42	0·42
309	−0·57	0·65	−0·78	0·75
505	0·19	0·18	0·33	0·28
2,0,10	0·30	0·23	0·47	0·46
408	0·39	0·38	0·63	0·72
506	−0·06	< 0·12	−0·10	< 0·12
1,0,11	0·07	< 0·12	0·11	< 0·12
600	0·47	0·38	0·74	0·59
601	0·04	< 0·12	0·08	< 0·12

* Experimental structure factors have been increased by $-2\cdot5\%$ at $-50°$ C. and by $0\cdot5\%$ at $-150°$ C. from original scale, in accordance with least-squares scale factor.

† These structure factors have been corrected for extinction; the uncorrected values are 2·21, 3·25, 1·73 and 2·85.

of the normal equations were inverted to yield the precision measures of the parameters.

In the case of both sets of data, only very small changes in position parameters occurred, but the

temperature factors changed significantly, and considerable asymmetry was indicated. The agreement factors decreased to 5·4% for −50° C. data and to 4·6% for −150° C. data. The latter figure includes extinction-corrected values, and unobserved reflections at one-half the minimum observable value. If extinction-affected and unobservable reflections are omitted, the agreement factor is 3·55%.

Table 3 lists the input and output least-squares parameters for the two sets of data. The temperature-factor coefficients are listed in the form $4\beta_{ij}/b_i b_j$, where β_{ij} is a coefficient in expression (1) and b_i is the corresponding reciprocal-axis length. In this form, they bear a close analogy to the conventional Debye–Waller B: for symmetric motion $4\beta_{11}/b_1^2 = 4\beta_{22}/b_2^2 = 4\beta_{33}/b_3^2 = B$ and $4\beta_{ij}/b_i b_j = 2B \cos \gamma_{ij}$, $i \neq j$, where γ_{ij} is the angle between reciprocal axes i and j.

Discussion

The quality of the agreement between experimental and calculated structure factors shown in Table 4 leaves little doubt that the half-hydrogen model is an essentially correct description of the long-range structure of ice. The excellence of the Fourier map which is based upon a sign determination using this model is equally good evidence. No evidence for lower symmetry than that of space group D_{6h}^4 was found. Thus it seems evident that a completely polar model of the Rundle type cannot be maintained. However, it is not possible to rule out entirely the existence of partially polar structures in ice on the basis of the diffraction data alone. One can conceive, for example, of a structure departing from the Pauling type by a tendency toward ordering of the protons in the O–H–O links parallel to the c axis. The maximum amount of such ordering allowed by the present data is roughly estimated at about 20%. However, since there is no substantial evidence requiring a polar structure, further examination of this possibility does not appear justified.

Interatomic distances and angles, as identified in

Table 5. *Interatomic distances and angles and their standard deviations**

Distances (Å)	−50° C.	−150° C.
O–O′	2·752±0·008	2·755±0·006
O–O″	2·765±0·0002	2·746±0·0002
O–D₁†	1·000±0·009	0·997±0·007
O–D₂†	1·007±0·005	0·997±0·004
D₁–D₂	1·635±0·012	1·625±0·009
D₂–D₂	1·648±0·009	1·632±0·006

Angles		
O′–O–O″	109° 33′± 9′	109° 18′± 7′
O″–O–O‴	109° 24′± 1′	109° 38′± 1′
D₂′–O–D₂	109° 52′±16′	109° 54′±15′
D₁–O–D₂	109° 6′±18′	109° 11′±13′

* The atoms are identified in Fig. 2. Standard deviations reflect parameter uncertainties only.
† This is the uncorrected O–D distance (see text).

Fig. 2, are listed in Table 5 along with standard error estimates. Correlated errors among the parameters, as given by the least-squares analysis, were sometimes
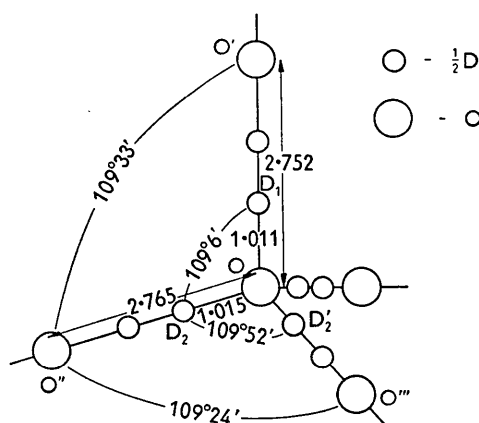

Fig. 2. Structural relationships in one tetrahedron of the ice structure. The distances and angles are those at −50° C.

appreciable and were taken into account. The error estimates reflect uncertainties in the parameters only, i.e., the unit-cell dimensions were assumed exact; thus some of the quantities, for example the O–O″ distance and the O″–O–O‴ angle, have unrealistically small errors listed. After allowance for uncertainties in the cell dimensions, there appears to be no significant change in any of the quantities with temperature. Upon comparing chemically equivalent but crystallographically non-equivalent distances and angles, only the pair of angles D₂′–O–D₂ and D₁–O–D₂ are possibly significantly different; here the differences of 46′ and 43′ at the two temperatures are approximately twice the combined standard deviations. At both temperatures deuterium atom D₂ lies, within about one standard error, on the corresponding O–O line.

The O–D distances reported in Table 5 require special consideration in view of the large thermal amplitudes of deuterium relative to oxygen. This motion results in an appreciable average angle of inclination of the O–D vector with respect to the mean O–D direction. The apparent distances listed in the table can thus be considered to represent the mean projections of the true distances. A reasonable estimate of the true distances d can be given by

$$d^2 = d_a^2 + (\overline{\mu_{D,\perp}^2} - \overline{\mu_{O,\perp}^2}) ,$$

in which d_a is the apparent or projected distance, and $\overline{\mu_{D,\perp}^2}$, $\overline{\mu_{O,\perp}^2}$ are the mean square thermal displacements of D and O perpendicular to the mean direction of O–D. A similar effect has been discussed for the C–C distance in benzene (Cox, Cruickshank & Smith, 1955). When this correction is made, the distances become

$$O–D_1 = 1·011 \text{ Å}, \quad O–D_2 = 1·015 \text{ Å} \quad \text{at} \quad -50° \text{C.},$$

and

$$O-D_1 = 1.008 \text{ Å}, \quad O-D_2 = 1.009 \text{ Å} \quad \text{at} \quad -150° \text{ C}.$$

The differences are not significant. The close equality of crystallographically non-equivalent distances is evidence against the possibility of preferential ordering of one set of hydrogen atoms.

Thermal parameters

The complete least-squares treatment carried out allows an unusually complete description of the thermal motion in ice. The temperature coefficients which are listed in Table 3 give immediate indication of asymmetry. It is to be noted that while the oxygen temperature motion is nearly symmetric, that of the deuterium atoms is decidedly asymmetric. The effect is somewhat more marked at the lower temperature. In order to examine the anisotropy more closely a transformation to principal axes of the thermal ellipsoid (Waser, 1955) was carried out. The results are shown in Tables 6 and 7. Principal-axis thermal parameters $B^{(r)}$ and root-mean-square displacements $\{\overline{\mu^{2(r)}}\}^{\frac{1}{2}}$ (which are related by $B = 8\pi^2\overline{\mu^2}$) at the two

Table 6. *Principal-axis coefficients and displacements*

Atom	−50° C. Principal axis No.			−150° C. Principal axis No.		
	(1)	(2)	(3)	(1)	(2)	(3)
	Values of $B^{(r)}$ (Å²)					
O	2·39	2·39	2·29	1·52	1·52	1·47
D_1	3·23	3·23	2·97	2·39	2·39	1·81
D_2	3·86	3·19	2·65	2·42	2·51	1·75
	Values of $\{\overline{\mu^{2(r)}}\}^{\frac{1}{2}}$ (Å)					
O	0·174	0·174	0·170	0·139	0·139	0·137
D_1	0·202	0·202	0·194	0·174	0·174	0·152
D_2	0·221	0·201	0·183	0·175	0·178	0·149

Table 7. *Components of the principal-axis vectors $\mathbf{q}^{(r)}$ of D at $2\bar{x}, \bar{x}, z$ resolved along the reciprocal axes $\mathbf{b}_i$*

	−50° C.			−150° C.		
	$\mathbf{q}^{(1)}$	$\mathbf{q}^{(2)}$	$\mathbf{q}^{(3)}$	$\mathbf{q}^{(1)}$	$\mathbf{q}^{(2)}$	$\mathbf{q}^{(3)}$
$\mathbf{b}_1$	1	−0·348	0·858	1	−0·188	1·500
$\mathbf{b}_2$	−2	0	0	−2	0	0
$\mathbf{b}_3$	0	1	1	0	1	1

temperatures are listed in Table 6. The orientations of the ellipsoids of O and D_1 are determined by their location on a symmetry axis. The orientation of the thermal ellipsoid for D_2 is described by listing components (Table 7), resolved along the reciprocal axes, of vectors directed along the principal-axis directions. The results at −150° C. are particularly striking. The vector $\mathbf{q}^{(1)}$ represents the principal axis required by symmetry to be perpendicular to the mirror plane, and thus parallel to direct crystal axis $\mathbf{b}$. Vectors $\mathbf{q}^{(2)}$ and $\mathbf{q}^{(3)}$ lie in the mirror plane. The vector $\mathbf{q}^{(3)}$ makes an angle of 109° 22′ with the z axis and is thus closely

parallel to the $O-D_2$ bond direction. The root-mean-square displacement along this direction is the smallest of the three, and the other two displacements are nearly equal. The near equality of corresponding $(\overline{\mu^2})^{\frac{1}{2}}$ values for the two types of deuterium is worthy of note. The principal root-mean-square displacements of deuterium relative to oxygen essentially along the bond directions* are 0·0655±0·016 Å for D_1 and 0·0597 Å for D_2. Assuming harmonic motion, approximate bond stretching frequencies may be calculated for $(O-D)_1$ and $(O-D)_2$ yielding the values of 2200±538 and 2660 cm.$^{-1}$ respectively, which are of reasonable magnitude. These gratifying results are an indication of the increased information obtainable from accurate diffraction data when complete refinement is undertaken.

The results at −50° C., where thermal motions are increased and parameters less well determined, are qualitatively similar to those at −150° C. 'but quantitatively less striking. Close equality between the thermal parameters of D_1 and D_2 is no longer maintained. Vector $\mathbf{q}^{(3)}$ is no longer closely parallel to the $O-D_2$ direction; it lies in the mirror plane and inclined 122° to the c axis, 13° to $O-D_2$, and an error analysis indicates this inclination to be significant. It would thus appear that some interaction other than central valence forces plays a role in fixing the local symmetry of thermal displacement of D_2 at −50° C. The displacement normal to the mirror plane, indicated by $B^{(1)}$, is now the largest principal displacement, suggesting librational motion of the water molecule about the c axis. The root-mean-square 'stretching' displacement of D_1 relative to oxygen at −50° C. is 0·0924 with a standard error of 0·028 and is thus not significantly different from that at the lower temperature. On the whole, these results suggest a tendency toward greater distinction between D_1 and D_2, noticeable in bond length and angle and in thermal parameters. That this tendency should appear at the higher temperature is somewhat surprising; however the reality of the effect may well be questioned.

Precision of the determination

It is of interest to consider briefly the magnitudes of errors associated with the present work. The overall measure of error used in the previous discussion, the agreement factor, reached the acceptably low value of 3·55% at −150° C. when doubtful reflections were omitted. However, based on the experimental standard errors assigned in the weighting scheme, the factor might have been expected to reach the neighborhood of 1·7%. We may make a somewhat better judgement of agreement by means of the function

$$\left(\sum_i \frac{w_i(F_o - F_c)^2}{m-n}\right)^{\frac{1}{2}},$$

_____

* Assuming the relative displacement is distributed independently of the position of O.

the standard deviation of an observation of unit weight estimated from the residuals. Here w_i is the weight of the ith observation, m is the number of observations and n is the number of parameters. For appropriately weighted data and normally distributed observational errors, the expected value of this function is unity. The values found in this work are 4·07 and 4·41 at $-150°$ C. and $-50°$ C. respectively. These deviations from unity are large, and in retrospect are believed to be indicative of under-estimation of the observational errors. The specimens used were unusually large, both in height and diameter, and because of manipulative difficulties were only approximately cylindrical. Under these circumstances, considerable errors in determination of structure factors, aside from those due to counting statistics, are conceivable. It is of course also possible that the discrepancy reflects an inadequacy of the model in terms of which the data were evaluated.

Diffuse neutron scattering

While the present data seem to rule out rather conclusively long-range ordering of deuterium, it cannot be said that the detailed nature of the disorder is known. Further evidence concerning the nature of the disorder should in principle be obtainable from analysis of the diffuse background scattering of ice. Several diffuse maxima were observed in the neutron scattering from heavy ice at both temperatures, and an attempt was made to map in reciprocal space the regions of high diffuse scattering. Examination of the zero level of [01.0] gave evidence of maxima which were characterized by the approximate reciprocal-lattice directions (103), (100) and (102) and $\sin \theta/\lambda$ equal approximately to 0·66, 0·63, and 0·57 respectively. An additional feature of the diffuse background was an isotropic component which decreased steadily with increasing angle. This pattern of diffuse scattering is not simply explained by considering only the main elements of disorder, i.e., the interactions between adjacent hydrogen sites on hydrogen bonds and the interactions within one oxygen tetrahedron. It appears not unlikely that inelastic scattering of neutrons may play a role in this effect.

Note added in proof, 4 *December* 1956.—Gränicher (1956) recently suggested the possibility of polar

domains within which the H atoms are ordered, these domains being randomly oriented with polar axis parallel and antiparallel to c. If the domains are large enough to diffract coherently (far smaller than the microstructure quoted) the neutron intensities would be those for the disordered model found. Rundle's 'non-classical, truly hexagonal' arrangement (Rundle, 1955) would also be incompatible with the observed intensities.

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