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The Structure of Ice II

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The stability of the high pressure ice forms discovered by Tammann and Bridgman at very low temperatures and atmospheric pressure has made it possible to obtain x-ray powder diffraction photographs of these forms. The experimental procedure is very briefly discussed. An analysis of the ice II diffraction patterns leads to a side-centered orthorhombic cell with $a=7.80\text{\AA}$, $b=4.50\text{\AA}$, and $c=5.56\text{\AA}$. This cell contains eight molecules, has the symmetry of space group V^s-C222_1 , and gives a value for the density of 1.21. The proposed arrangement of the hydrogen atoms

indicates that the transition from ice I to ice II breaks up the water molecule, and that ice II is an ionic crystal. According to the model described the effect of a pressure of 2100 atmospheres in forming ice II is: (1) To decrease the packing volume of the oxygen ion approximately three percent; (2) To break down the open ice I structure by a slipping of the oxygen ion layers relative to each other; (3) To give a four-coordinated structure where each oxygen is surrounded by a badly distorted tetrahedron of oxygen ions.

INTRODUCTION

THE existence of polymorphous ice forms at high pressures was first discovered by Tammann,¹ and was later thoroughly investigated by Bridgman² who discovered several additional forms. As these ice forms are not stable at ordinary pressures and temperatures their structure has not as yet been determined by x-ray methods. A knowledge of the crystal structure of the various high pressure ice forms would provide valuable information regarding the following points:

1. The effect of pressure on the coordination of the water molecule.
2. The effect of pressure on the angle between the OH directions of the water molecule.
3. The mechanism of the solid-solid reaction that takes place when a phase line separating two ice forms is crossed.

The present investigation was undertaken to determine the crystal structure of the different ice forms by x-ray diffraction methods.

EXPERIMENTAL WORK

The pressure-temperature range over which each ice form is stable is shown in Fig. 1 taken from Bridgman's paper. A detailed description of the technical difficulties involved, and the methods devised to overcome them will be made in a separate paper which will appear in the

Review of Scientific Instruments. A brief account will be given here.

If the temperature of any high pressure ice form is maintained sufficiently low it will remain stable at ordinary pressures indefinitely, and consequently can be irradiated with x-rays outside the press. The problem of extracting the high pressure ice crystal from the press was solved by Professor Bridgman, at whose suggestion this work was undertaken. The crystal was frozen under pressure, and before releasing the pressure the lower part of the press was immersed in liquid air. The crystal could then be removed without reverting to ice I.

The x-ray diffraction camera was of the standard powder design modified:

1. To maintain the crystal temperature near that of liquid air during exposure.

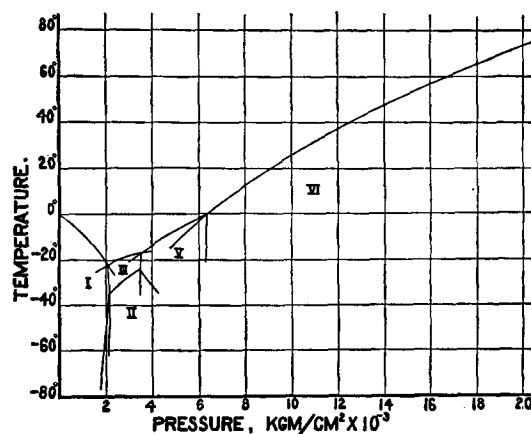


FIG. 1.

¹ Tammann, *Kristallisieren und schmelzen* (Barth, Leipzig, 1903), pp. 315-344.

² P. W. Bridgman, *Proc. Am. Acad.* **47** (1912).

2. To permit rapid insertion and centering of the crystal.

The actual crystal temperature during exposure—as measured by a thermocouple—was -155°C , and after some practice it was found possible to center and insert the crystal in the camera in from ten to fifteen seconds. The time of stability before a crystal would revert to ice I upon removal from liquid air was about twelve seconds.

With the exception of ice II it was found necessary to grind each crystal under liquid air in order to obtain good powder patterns. Attempts to form small crystal fragments by crossing the solid-solid phase lines several times were not very satisfactory.

The camera was calibrated in two different ways:

1. With an ice I diffraction pattern using Barnes's² data as a standard.
2. With a NaCl-gum tragacanth diffraction pattern.

Both calibration patterns were obtained in exactly the same way as the high pressure crystal patterns. These two methods gave identical calibration curves within the ordinary limits of experimental error. Cu $K\alpha$ radiation filtered through nickel was used to irradiate the crystal.

The possibility of frost forming on the outside of the high pressure crystal made it necessary to test for the presence or absence of ice I lines on the high pressure ice films. The complete absence of ice I lines on the patterns of the other ice forms was inferred from the following observations:

1. The NaCl-gum tragacanth pattern showed no ice I lines.
2. An empty cellophane cylinder exposed under the usual conditions showed no powder lines.
3. A single crystal rotation photograph of ice VI showed no trace of any powder lines.

It is also possible that the diffraction patterns might be produced by a mixture of two kinds of crystals as a result of the solid-solid reaction not going to completion after crossing a phase line. To eliminate this possibility patterns were obtained from several crystals of each ice form, each crystal being formed by crossing a different phase line into the desired region. In this way it was easy to identify the lines that were characteristic of a particular ice form.

THE CRYSTAL STRUCTURE OF ICE II

Two methods of computing the density from the Bridgman² data were used. In the first of these it was assumed that ice II would show the same relative change of volume over the pressure range 2100–1 atmospheres as does ice I. Temperature-volume relations were neglected. In the second method the ice II compressibility-pressure curve was extrapolated to one atmosphere, whence the density could be computed from the average compressibility. Both of these methods gave values of approximately 1.15 for the density, which value is probably accurate to within ten percent.

An excellent match between the observed and calculated interplanar spacings can be obtained on a hexagonal lattice with an axial ratio of 1.24. This leads to a unit cell 4.50 by 5.56 Angstroms, containing four molecules and giving a density of 1.21, a value which differs by approximately five percent from the extrapolated Bridgman value. However, no space group of the hexagonal system permits a distribution of oxygen atoms which predicts intensities in agreement with those observed. But it is possible to arrange the four atoms on a hexagonal lattice in such a way as to obtain a good fit between the observed and calculated intensities. This arrangement—which does not have the trigonal symmetry required of all hexagonal space groups—is shown projected on the xy plane in Fig. 2. As appears in the diagram the oxygen atom distribution may also be represented by an orthorhombic lattice whose axial ratios are 1.73 : 1 : 1.24. The symmetry is that of space group V^3-C222_1 , and there are eight molecules in a unit cell of dimensions $a=7.80\text{\AA}$, $b=4.50\text{\AA}$, and $c=5.56\text{\AA}$. The oxygen atoms appear in the following positions:

$$\begin{array}{ll} xyz; & x\bar{y}\bar{z}; \\ x+\frac{1}{2}, y+\frac{1}{2}, z; & x+\frac{1}{2}, \frac{1}{2}-y, \bar{z}; \\ \bar{x}, y, \frac{1}{2}-z; & \bar{x}, \bar{y}, z+\frac{1}{2}; \\ \frac{1}{2}-x, y+\frac{1}{2}, \frac{1}{2}-z; & \frac{1}{2}-x, \frac{1}{2}-y, z+\frac{1}{2}; \end{array}$$

where the best agreement with observed intensities is obtained for $x=0.167$, $y=0.205$, and $z=0.178$. The calculated and observed interplanar spacings and intensities are shown in Table I. Each oxygen atom is surrounded by a badly distorted tetrahedron of oxygen atoms,

² W. H. Barnes, Proc. Roy. Soc. **A125**, 670 (1929).

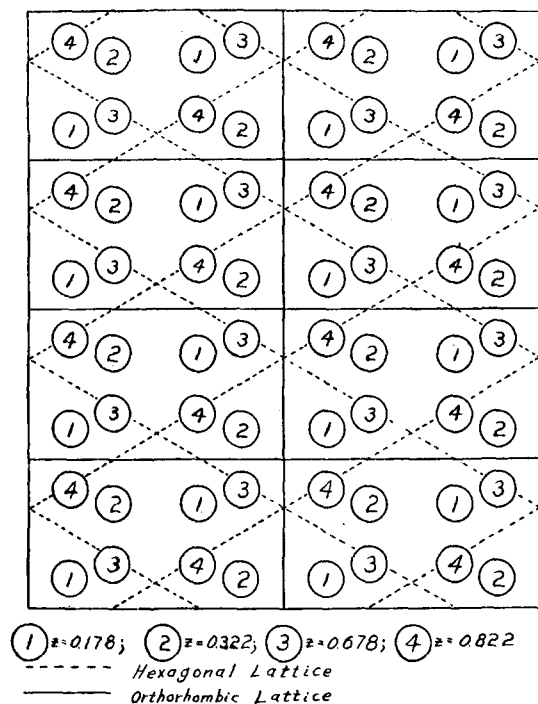


FIG. 2. Oxygen atoms—ice II.

giving a coordination of four as in ice I. The number and distance of various oxygen neighbors is shown below.

No. neighbors	4	2	1	2	6	2
Distance (Å)	2.71	3.09	3.31	4.23	4.50	4.65

This compares with four neighbors at 2.74Å and thirteen at 4.47Å for ice I. This shows the increased density of ice II to be the result of a relatively small change in nearest neighbor distances of ice I, i.e., actual ionic compression, and a considerable decrease in the ice I next nearest neighbor distances, i.e., geometrical compression.

The assignment of the hydrogen atom positions is necessarily arbitrary, since no x-ray evidence is available regarding this point. It is not possible to follow the procedure of Bernal and Fowler⁴ with ice I in assigning positions to the hydrogen atoms in the ice II structure. The distribution of oxygen atoms is such that the angle between the OH directions cannot be made the same for all the oxygen atoms, and at the same time a reasonable structure obtained. Consequently, it

⁴ Bernal and Fowler, J. Chem. Phys. **1**, 515 (1933).

TABLE I.

<i>hkl</i>	<i>d</i> (calc) (Å)	<i>d</i> (obs) (Å)	<i>I</i> (calc)	<i>I</i> (obs)	<i>hkl</i>	<i>d</i> (calc) (Å)	<i>d</i> (obs) (Å)	<i>I</i> (calc)	<i>I</i> (obs)
110	3.90				131	1.43			
200	3.90	3.8	33.7	v.s.	511	1.43			
111	3.20				313	1.43	1.43	4.6	m.
201	3.20	3.0	81.4	v.v.s.	023	1.43			
002	2.78	2.7	17.0	s.	421	1.43			
020	2.26				223	1.34	1.34	3.4	m.
202	2.26				403	1.34			
112	2.26	2.19	52.1	v.s.	114	1.31			
310	2.26				204	1.31			
311	2.09				600	1.30			
021	2.09	2.10	43.5	v.s.	330	1.30	1.29	9.2	s.
400	1.95				422	1.30			
220	1.95	1.94	5.9	m.	512	1.30			
221	1.84				132	1.30			
401	1.84	1.85	7.2	m.	331	1.27	1.26	1.3	m.
022	1.75				332	1.18			
312	1.75	1.74	3.7	m.	314	1.18	1.18	0.5	w.
113	1.68				024	1.18			
203	1.68	1.70	6.7	m.	133	1.15			
222	1.60				513	1.15	1.14	2.1	m.
402	1.60	1.59	4.4	m.	423	1.15			
510	1.48								
420	1.48	1.46	1.6	m.					
130	1.48								

is necessary to assume that the ice I-ice II transition breaks up the water molecule, and that the ice II crystal is made up of oxygen and hydrogen ions which do not form molecules. The simplest way to build up such a structure is to assume that each hydrogen ion lies on a line joining the center of an oxygen ion to the center of one of its nearest neighbors, and further that each hydrogen ion lies midway between the neighboring oxygen centers. This arrangement gives the necessary 16 ions of hydrogen per unit cell, is consistent with the accepted value for the O—H—O packing distance, and satisfies all the symmetry requirements of space group $V^s - C22_1$. The coordinates obtained in this way for the hydrogen ions are as follows:

$$u00; \bar{u}0\frac{1}{2}; u+\frac{1}{2}, \frac{1}{2}, 0; \frac{1}{2}-u, \frac{1}{2}, \frac{1}{2}, \text{ where } u=0.167; \\ 0u\frac{1}{4}; 0\bar{u}\frac{3}{4}; \frac{1}{2}, u+\frac{1}{2}, \frac{1}{4}; \frac{1}{2}, \frac{1}{2}-u, \frac{3}{4}, \text{ where } u=0.250; \\ xyz; x\bar{y}\bar{z}; \bar{x}, y, \frac{1}{2}-z; \bar{x}, \bar{y}, z+\frac{1}{2}; x+\frac{1}{2}, y+\frac{1}{2}, z; \\ x+\frac{1}{2}, \frac{1}{2}-y, \bar{z}; \frac{1}{2}-x, y+\frac{1}{2}, \frac{1}{2}-z; \frac{1}{2}-x, \frac{1}{2}-y, z+\frac{1}{2},$$

where $x=0.250$, $y=0.455$, $z=0.250$.

A projection on the xy plane of this arrangement is shown in Fig. 3.

The angle between the OH directions of the water molecule, which Mecke's⁵ measurements on steam and Barnes³ ice I data give as 103°–107°, loses its significance in this structure. For four of the oxygen atoms of the ice II structure the H—O—H angle is 103°, but the departure from this value for the other four atoms is large.

⁵ Mecke and Baumann, Physik. Zeits. **33**, 833 (1932).

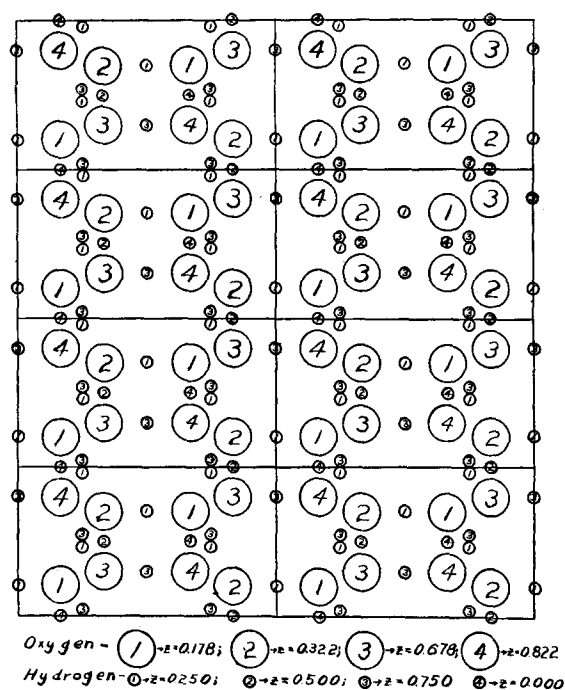


FIG. 3. Atomic distribution—ice II.

The change from ice I to ice II is, according to the model proposed, a slipping of adjacent oxygen ion layers, as shown in Fig. 4. If, in Fig. 2 the layers marked 3 and 4 were moved so as to make the xy coordinates of 3 and 2, and 4 and 1 coincide the resulting structure would be that of ice I. The mechanism of the ice I-ice II reaction can thus be pictured as a slipping of oxygen ion layers accompanied by a hydrogen displacement, as a result of the electrostatic attraction between the hydrogen and oxygen ions. The extent to which this slipping takes place is determined by the repulsive forces between the oxygen ions which are next nearest neighbors. In Fig. 3 this would mean the repulsive forces between the oxygen ions marked 1 and 3, and those marked 2 and 4. The proposed model places no hydrogen atoms between these next nearest neighbors, and consequently the effective distance of closest approach will be much larger than for the 2.71 Å nearest neighbor distance.

Additional evidence as to the reasonableness of the assumption that the water molecule is broken up in the course of the ice I-ice II transition is furnished by some recent, and as yet unpublished

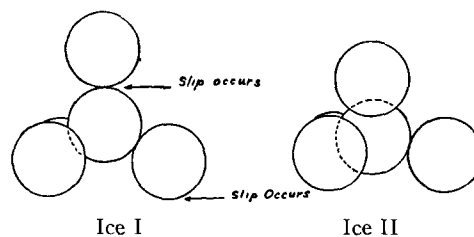


FIG. 4. Ice I-ice II reaction.

work of Professor Bridgman. He found that a high pressure plus a shear stress applied to lead oxide reduced it to pure lead. The reduction was purely a mechanical disruption of the PbO_2 molecule, no thermal effect being possible.

The only other analysis of a high pressure crystal that has appeared so far is the black phosphorus analysis of Hultgren, Gingrich, and Warren.⁶ In their solution the bond angles of phosphorus were found to fit the expected near tetrahedral values for bond angles of the lighter elements. However, black phosphorus contains but a single kind of atom, and further is stable under ordinary conditions whereas ice II satisfies neither of these conditions.

It is of interest to calculate what portion of the volume decrease in the ice I-ice II change is due to a difference in packing, and what portion is due to a redistribution of ions. The x-ray measurements give the O-H-O packing diameter as 2.71 Å, a decrease of 0.03 Å from the 2.74 Å value of ice I. This represents a decrease in molecular volume—assumed to be spherical—of 3.4 percent. Some estimate as to the reasonableness of this result can be obtained by assuming—as suggested by Bernal and Fowler⁴—that the volume change of any one ice over its range of pressure stability represents molecular compression. Then according to Bridgman's² data for ice I there would be a three-percent decrease in packing volume upon increasing the pressure 2000 atmospheres. The volume change on going from ice I to ice II is 22.3 percent at atmospheric pressure according to the x-ray measurements, and is 20 percent at 2000 atmospheres according to the Bridgman data. The difference between these volume changes, 2.3

⁶ Hultgren, Gingrich and Warren, J. Chem. Phys. 3, 351 (1935).

percent, corresponds roughly to the three-percent change in packing volume over 2000 atmospheres. The stability of ice II at very low temperatures would thus seem to be due to a thermal contraction of the oxygen ion of the same order of magnitude as the volume change under 2000 atmospheres pressure. Accordingly, the density obtained from the x-ray measurements is not necessarily the same as that under pressure in the press. As both the phase diagram of Bridgman² and the low temperature ice I measurements of

Barnes³ show, the thermal contraction is not in itself sufficient to cause the formation of ice II. The expenditure of external work is necessary to change the OH bond angles of ice I. This is in agreement with the giving off of latent heat during the course of the ice I-ice II reaction.

Further information regarding the effect of pressure on the water molecule can be obtained from the crystal structure of ice III. The results of the analysis of the ice III photographs already obtained will appear in the near future.

JANUARY, 1936

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Studies on Glass

XII. Some New Heat Capacity Data for Organic Glasses. The Entropy and Free Energy of *dl*-Lactic Acid

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(Received October 14, 1935)

Heat capacity measurements by the Nernst method have been made upon samples of secondary butyl alcohol and 3-methylhexane in the glassy and liquid condition and upon a sample of *dl*-lactic acid (1) in an incompletely crystallized state, (2) in the form of an *acid* glass and liquid, and (3) in the form of a *mixed* glass and liquid. From these results the specific heats and heat of fusion of pure crystalline *dl*-lactic acid also have been derived. The data for the

several glasses and undercooled liquids show a rapid rise from the heat capacity characteristic of a crystalline solid to that for the liquid state within a transition region of about 10° and the nature of this transition region has been discussed. A calculation of the molal entropy and free energy of formation of liquid *dl*-lactic acid at 298.1°K yields 45.9 (± 1.0) e.u. and $-124,300 \pm (2300)$ cal., respectively.

IN previous studies¹ dealing with organic glasses heat capacity data have been presented for ethyl alcohol, *n*-propyl alcohol, propylene glycol, and glucose, and for two mixed glasses or solutions containing glycerol and glucose and propylene glycol, glycerol and glucose, respectively. The data showed in every case a marked increase in heat capacity within a comparatively small temperature interval or *transition region*, the rate of increase being somewhat less rapid in the mixed glasses than with the pure substances. The materials represented in these earlier studies, however, were all primary alcohols or polyhydroxy compounds; and accordingly it seemed desirable to extend the measurements to other

types of substances. In the present study specific heat determinations have been made upon secondary butyl alcohol, *dl*-lactic acid, and 3-methylhexane—i.e., upon a typical secondary alcohol, a hydroxy acid, and a paraffin hydrocarbon. These substances all form stable glasses on cooling from the liquid state, although the lactic acid may also be obtained in the crystalline condition. It is interesting to note that in each case the molecule contains an asymmetric carbon atom and that the materials involved in the present study were in reality mixtures of equal amounts of the dextro and laevo forms.

MATERIALS

A very pure sample of secondary butyl alcohol was kindly prepared for us by H. E. Buc of the Standard Oil Development Company. Its boiling range was 99.52–99.55°C.

* Shell Research Fellow at Stanford University for the academic year 1930–31.

¹ (a) Parks and Huffman, *J. Phys. Chem.* **31**, 1842 (1927); (b) Parks, Huffman and Cattoir, *J. Phys. Chem.* **32**, 1366 (1928); (c) Parks, Thomas and Gilkey, *J. Phys. Chem.* **34**, 2028 (1930).