

scattering phenomena. The latter would involve the development of better and more readily applicable models for treating, for example, thermal diffuse scattering, and a more general willingness to take the trouble to apply these models routinely.

I wish to thank Professor Ivar Olovsson for his support and interest in this work. Financial support from the Swedish Natural Science Research Council is also gratefully acknowledged.

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## A Molecular-Packing Analysis of the Crystal Structures of Ice

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(Received 16 July 1984; accepted 7 November 1984)

### Abstract

A rationalization of the structures of the crystalline phases of ice has been attempted, through lattice-energy calculations based upon the ST2 potential model for interaction between water molecules. Ordered models for H-atom coordinates were assumed, where these are not experimentally available. Calculated energies were broadly consistent with the phase diagram, except for ice I and ice V which both calculate as being more stable than is observed. The calculated energy for ice VIII is highly dependent upon the relative directions of the polarity of the two independent hydrogen-bond networks.

### Introduction

It has been demonstrated in a number of studies of the crystal structures of rigid molecules (Kitaigorodskii, 1970; Williams & Starr, 1977) that the observed structure corresponds to those values of the cell and molecular parameters for which lattice energy is a minimum. Such studies normally assume knowledge of the space group and the number of molecules per cell, and only in that limited sense could they be described as having predicted the crystal structure. Prediction without such restriction on the basis of calculated energy alone would be a formidable computational task, and has only been attempted in

special cases wherein possible alternative models of molecular interaction can reasonably be predefined (Hagler & Leiserowitz, 1978; Dauber & Hagler, 1980). A related problem exists where pressure-dependent polymorphism occurs; it should be demonstrable that the low-pressure form is indeed that for which lattice energy is greatest (most negative), but that the  $p \cdot \Delta v$  work term would stabilize the alternative at the appropriate pressure. This has been so demonstrated for the case of benzene (Hall, Starr, Williams & Wood, 1980). A more complex problem of the same kind concerns the various structures of ice, the phase diagram for which is reproduced in Fig. 1. This paper describes an attempt to rationalize the structures of ice on the basis of lattice-energy calculation, the ST2 potential model (Stillinger & Rahman, 1974) for interaction between water molecules being assumed.

The methods of packing analysis (Kitaigorodskii, 1970; Williams, 1972) assume essentially that the structure is ordered; they assume implicitly that the structure of minimum lattice energy is also that of minimum free energy, *i.e.* that the difference in entropy between alternative ordered structures will not be great. The problem relating to ice is made more difficult by the fact that in most phases the protons are not ordered, *i.e.* the Pauling (1935) rules do not specify a unique arrangement with regard to the orientation of the molecules, which appear to be wholly or partly random over various alternatives (Eisenberg & Kauzmann, 1969). In this sense, disorder exists in all of the higher-temperature phases *Ih*, III, VI and VII, as well as the cubic structure *Ic* which is formed under some non-equilibrium conditions. Phase V is partially disordered. Phase II is ordered, while phases III and VII become ordered at lower temperatures, and are then known as IX and VIII respectively. Phase IV is a metastable form which has been reported for heavy ice within the stable region

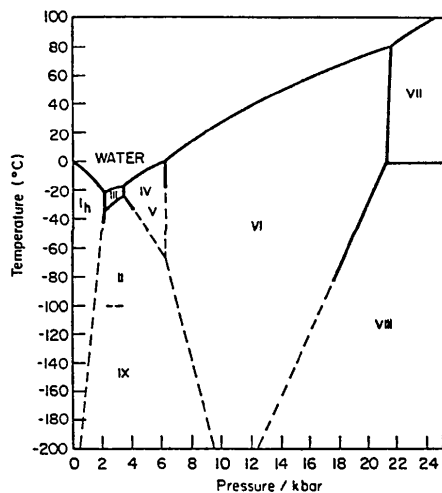


Fig. 1. Phase diagram of ice (von Hippel & Farrell, 1973) (1 kbar =  $10^8$  Pa).

of V, but its existence has not been confirmed. The ideal ordered structure is not then always known; reasonable postulates of the H-atom arrangement can be made, but there must remain uncertainty as to whether any such is indeed the minimum-energy structure, and also as to the difference in molecular interaction energy between the ideal ordered and the actual disordered phases. The basis of the prediction that ice *Ih* would be disordered (Pauling, 1935) was the expectation that such difference would not be great; presumably it will not be greater than 0.8 e.u. (1 e.u. =  $4.2 \text{ J K}^{-1} \text{ mol}^{-1}$ ) (Giauque & Ashley, 1933), the known entropy of disorder in ice *Ih*.

### Computational

The ST2 potential model (Stillinger & Rahman, 1974) for the water molecule assumes a neutral central O atom, surrounded at exact tetrahedral angles by two positive charges of 0.2357 e at distance 1.0 Å from the central atom and two corresponding negative charges at distance 0.8 Å. The interaction between two molecules is the sum of a Lennard-Jones type 6-12 term between the O atoms, and the electrostatic interactions, the latter being modified by a 'switching function' to prevent catastrophes should molecules approach too closely. The switching function  $S$  is of the form, where  $r$  is the distance between O atoms,  $R_L = 2.0160$ ,  $R_U = 3.1287$  Å:

$$\begin{aligned} r \leq R_L, \quad S &= 0 \\ R_L < r < R_U, \quad S &= \frac{(r - R_L)^2 (3R_U - R_L - 2r)}{(R_U - R_L)^3} \\ R_U \leq r, \quad S &= 1. \end{aligned}$$

For each ice model structure, ST2 O atoms were located at the observed O positions, and the orientation of the ST2 molecule adjusted to give best least-squares fit between the positive charges and the observed or postulated H positions. Energy was calculated as the sum of interactions between all molecules within 6 Å of those in the asymmetric unit, using the molecular-packing program *PCK6* (Williams, 1972), modified to include the switching function, and to enable non-zero fractional coordinates for molecular centres to be held constant. It should be noted that the program embodies routines which effect convergence of the  $r^{-6}$  and  $r^{-1}$  sums (Williams, 1971). Energy was minimized with respect to all independently variable lattice parameters and rigid-body molecular parameters.

For every ice phase except II, the symmetry of the O-atom arrangement (and the apparent symmetry of the disordered structure) is higher than that which the protons must display when they are ordered. In all calculations the positional parameters of the O atoms, and the cell parameters where appropriate, were correlated so as to maintain the symmetry of

Table 1. *Results of lattice-energy calculations*

Phase	Ih			Ic		II		III/IX		
	Obs.	Calc.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	
Temperature (K)	263			143		213		110		
Cell parameters (Å)	$a = 4.519$ $c = 7.363$	$4.60 (\times\sqrt{3})$ 7.44	4.48 7.52	4.50 7.35	$a = 6.36$	6.35	$a = 12.92$ $c = 6.23$	13.31 6.27	6.73 6.83	6.94 7.15
Molecular volume (Å <sup>3</sup> )	32.6	34.0	32.9	32.2	32.0	25.0	26.7	25.8	28.7	
O...O separation (Å)	2.76	2.80-2.81	2.75-2.82	2.76-2.77	2.75	2.75-2.82	2.76-2.89	2.76-2.81	2.77-2.86	
Lattice energy (kJ mol <sup>-1</sup> )		59.9	61.3	61.9		61.9	57.5		56.8	
Energy components (kJ mol <sup>-1</sup> )										
$r^{-12}$		10.2	10.1	10.5		10.8	8.3		8.3	
$r^{-6}$		-6.5	-6.4	-6.6		-6.7	-7.3		-6.6	
$r^{-1}$		-63.6	-65.0	-65.8		-66.1	-58.5		-58.4	
Phase	V		VI		VII/VIII					
	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Calc.			
Temperature (K)	110		98		223					
Cell parameters (Å, °)	$a = 9.27$ $b = 7.54$ $c = 10.35$ $\beta = 109.2$	9.28 7.62 10.47 107.9	$a = 6.27$ $c = 5.79$	6.13 5.92	6.16 5.88	$a = 6.60$	6.43	6.60	6.52	
Molecular volume (Å <sup>3</sup> )	24.3	23.9	22.8	22.3	22.3	18.0	16.6	18.0	17.4	
O...O separation (Å)	2.77-2.86	2.73-2.96	2.80-2.81	2.75-2.81	2.76-2.82	2.86	2.79	2.86	2.83	
Lattice energy (kJ mol <sup>-1</sup> )	57.8			55.3	55.0		64.5	55.0	57.8	
Energy components (kJ mol <sup>-1</sup> )										
$r^{-12}$		11.3		10.6	9.8		20.9	15.3	17.6	
$r^{-6}$		-8.4		-9.0	-8.7		-14.8	-12.7	-13.5	
$r^{-1}$		-60.7		-56.9	-56.0		-70.6	-57.7	-61.8	

the O atoms. The remaining positional and cell parameters, and the molecular orientation parameters were considered as independent. Where the H-atom arrangement of the ordered phase is not experimentally known, models were assumed as discussed below.

Ice Ih shows apparent hexagonal symmetry, with four molecules per unit cell. The simplest ordered structure which fully retains hexagonality has a cell three times this size (Bernal & Fowler, 1933); this structure is designated hereafter as ice Ih<sub>h</sub>. If hexagonal symmetry is required only of the O atoms there are two possible ordered H arrangements which retain the four-molecule cell (Shimaoka, 1960). Overall, these have in one case diad symmetry, in the other no symmetry at all, and they are referred to respectively as ice Ih<sub>m</sub> and Ih<sub>t</sub>. These three were chosen as examples of ordered Ih structures; there is an unlimited number of others which could have been proposed.

Ice Ic is cubic, with eight molecules to the cell. The simplest ordered structure retains the same cell but is tetragonal in symmetry (Shimaoka, 1960), and only this model was considered. For ice II (Finch, Rabideau, Wenzel & Nerenson, 1968) and ice IV (Kamb & Prakash, 1968) the H positions are known experimentally. For ice V (Hamilton, Kamb, La Placa & Prakash, 1969), the H array is partly ordered and the occupancy is known, and an arrangement of high probability was chosen which retained the minimum unit cell. This had diad symmetry only, and contained seven independent molecules. The structure of ice VI is normally described (Kamb, 1965) in terms of two

interpenetrating arrays of water molecules, independent of one another with respect to their hydrogen bonding; various ordered arrays are possible, all of which are polar, and one such was chosen. It was not known whether the polarity of the independent chains should be parallel or opposed, and both models were tested. These are designated ice VI<sub>p</sub> and VI<sub>o</sub> respectively. Ice VIII is ordered (Whalley & Davidson, 1965), but the H arrangement is not known experimentally; it is again described in terms of independent interpenetrating structures, each being as for ice Ic (Kamb & Davis, 1964). For each the same proton array as in ice Ic was assumed. There are three possibilities for the mutual polarities of the two ordered structures, that they parallel, opposed or mutually perpendicular (ice VIII<sub>p</sub>, VIII<sub>o</sub>, VIII<sub>mp</sub>), and all were tested. The results are listed in Table 1.

### Discussion

The enthalpy of sublimation of ice at 0 K is 47.3 kJ mol<sup>-1</sup>; corrected for zero-point motion, the lattice energy at 0 K is 56.0 kJ mol<sup>-1</sup> (Eisenberg & Kauzmann, 1969). The present calculations do not explicitly include thermal motion but, as the parameters of the ST2 model were optimized to fit the properties of liquid water (Stillinger & Rahman, 1974), the results must be more relevant to room-temperature conditions. Estimation of lattice energy from experiment is then more difficult, but the calculated values for the ice Ih models, 59.9-61.9 kJ mol<sup>-1</sup>, are of appropriate magnitude. Of the three alternatives, ice Ih, has the highest (most negative) lattice

energy. As this model also most accurately reproduces the observed cell parameters, it may be the most appropriate representation of ordered ice *Ih*. It is notable also that the other models predict lattice energy less than that calculated for ice *Ic*. For ice *Ih*, the two are equal; this study then is no more successful than others have been in explaining the relative instability of the cubic structure. The suggestion (Bjerrum, 1952; Pitzer & Polissar, 1956) that secondary neighbour interactions would favour ice *Ih* over *Ic* if there were some degrees of order in the structures is scarcely supported by these calculations.

The advantage of the ideally tetrahedral hydrogen bonding in ice *Ih*, as opposed to the distorted arrangements in the adjacent phases II and III, is evident from the calculated lattice energies. As entropy effects must favour *Ih* over II, and should be small between *Ih* and III, the difficulty is not in explaining the existence of ice I at atmospheric pressure, but rather the transition to the other phases at pressures as low as 200 MPa. The  $p\Delta v$  work terms are less than 1 kJ mol<sup>-1</sup>, and the calculated energy differences are much greater. Notwithstanding this, the relative lattice energies of II and III appear to be appropriate; if the entropy of disorder is assumed to be 0.8 e.u. (Giauque & Ashley, 1933), or 0.8 kJ mol<sup>-1</sup> at 240 K, then disordered ice III could well be more stable than ordered ice II at 240 K, but not at lower temperature. The energy calculated for ice VI is consistent with that for ice II and ice III, in that it is slightly lower (less negative) but such that the  $p\Delta v$  contribution should stabilize the phase at 600 MPa. The calculated energy for ice V is, however, too high to fit this sequence. It may be relevant that in this structure the symmetry is lower, the number of variable parameters much higher; as with the models for ice I, higher symmetry appears not to lead to advantage. For ice VIII the three models give markedly different results. Structure VIII<sub>o</sub>, that for which the polarities of the two substructures are opposed, is stable when the cell size equals that observed and its energy is comparable with that for ice VI. By contrast the structure VIII<sub>p</sub>, with parallel polarities refines to a distinctly shorter cell edge, and to a much higher (more negative) energy; not only is this structure much more stable than either of those tested for ice VI, but it is 2.5 kJ mol<sup>-1</sup> more stable than for any model of ice *Ih*. Structure VIII<sub>mp</sub> gives intermediate results. If the ST2 potential model is valid under these

highly compressed packing conditions, it is clear that the parallel structure cannot be correct, as ice VIII is only stable at atmospheric pressure at temperatures below 80 K. Little is known of the mechanism of the VII → VIII ordering process, but the two independent hydrogen networks may well order independently, whence VIII<sub>mp</sub> would be the most probable representation. The alternative models of ice VI do not show the same variation in energy as do those of ice VIII, reflecting the fact that the individual molecular dipoles are aligned to a lesser extent in the ordered network in VI, and perhaps suggesting why it is that ice VII orders at low temperatures but ice VI does not.

Program PCK6 was kindly supplied by Dr D. E. Williams. Fig. 1 is reproduced from von Hippel & Farrell (1973).

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