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# Energetics of hydrogen ordering in ice

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## Abstract

Coulomb energies of ferroelectric and antiferroelectric ordering of protons in ice Ih and Ic are compared for unit cells containing eight water molecules. The lowest energy is obtained for antiferroelectric ordering in both the hexagonal and cubic structures, with the hexagonal energy per molecule being lower by about  $2 \times 10^{-4} q^2/R$ , where  $q$  is the net charge on the hydrogens and  $R$  is the oxygen–oxygen nearest-neighbour distance. The hexagonal ice energy is thus lower by about 0.3 meV per molecule, in the comparison of the lowest states. However, many of the possible configurations in the hexagonal eight-molecule cell have energies higher than the lowest energy of cubic ice. For both hexagonal and cubic structures, energy favours antiferroelectric hydrogen ordering, while entropy favours the weakly ferroelectric arrangements. An appendix considers Coulomb energies in cubic and hexagonal diamond, and shows that the electrostatic energy is lower in the naturally occurring cubic form. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Coulomb energy; Hydrogen ordering; Ice; Diamond

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## 1. Introduction

The author has previously explored the electrostatics of proton arrangements in cubic ice Ic [1]: in a unit cell of eight water molecules there are 90 possible configurations of the hydrogen nuclei, but degeneracy of the Coulomb energy reduces these to four different classes, of which the antiferroelectric structure has the lowest energy, and the fully ferroelectric structure has the highest energy. Here we consider the energies of ferroelectric and antiferroelectric arrangements in hexagonal ice Ih, and compare the results with those for cubic ice Ic.

Both Ih and Ic are tetrahedrally hydrogen bonded, with very similar (if not identical) bond lengths and densities [2,3]. The proton disorder postulated by Pauling [4] is in agreement with the measured residual entropy [2,3]. However, there are energy differences (in the meV range) between the various proton arrangements in cubic ice Ic [1], and ice Ih doped with KOH undergoes a transition to an ordered phase at 72 K [5–8]. Here we calculate the Coulomb energies of ferroelectric and antiferroelectric configurations in ice Ih, on the assumptions that (i) each proton is at the same fraction  $f$  of the oxygen–oxygen distance  $R$  from the nearest oxygen, and (ii) that the net charge on each hydrogen is  $q$  and on each oxygen  $-2q$ , in all configurations satisfying the ice rules [9]. The electrostatic energies are expressed as  $q^2/R$  times

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a function of  $f$ . The range of values of  $f$  is 0.31 to 0.37 [10,11], while an even larger range of  $q$  values, namely  $0.41|e|$  to  $0.865|e|$ , has been used in computer simulations of water and ice [12,13]. The qualitative conclusions in Ref. [1] and this paper about relative energies of various configurations are unaffected by changes in the choice of  $f$  or  $q$ , although the numerical magnitudes of the energies are affected.

## 2. The geometry of three unit cells

The calculations were done for two 8-molecule unit cells both related to the Kamb cell [14], illustrated in Fig. 1. The Kamb (k) cell contains 16 water molecules. The other two cells contain eight water molecules. One (h) is half of the Kamb cell, the other (j) is related to the h cell by interchange of the  $x$  and  $y$  coordinates (or a translation in the  $xy$  plane and a  $60^\circ$  rotation about the  $z$ -axis). There are more proton configurations possible in a superlattice composed of k cells than in superlattices made up of h or j cells, but for the antiferroelectric and fully ferroelectric arrangements the three cells

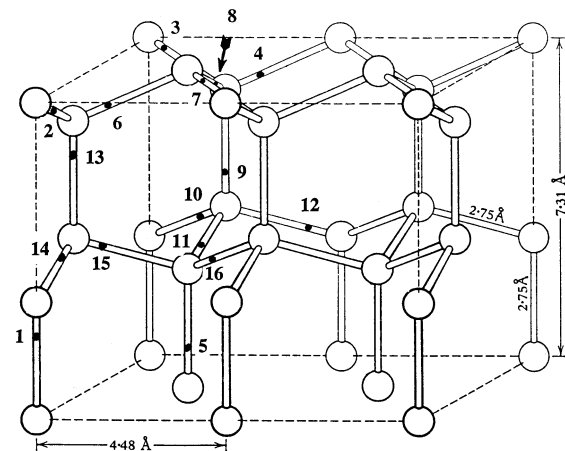


Fig. 1. The Kamb cell for hexagonal ice Ih, with 16 water molecules. One-half of this (the h cell) has eight oxygens and 16 hydrogens. The protons in the h cell are numbered; the configuration shown is [6 2 3 6] in the scheme defined in Section 4. The cell dipole value is  $q(1 - 2f)(-a, 0, 0)$ ; the energy is the same as that of the configuration [1 4 4 2] listed in the table of Section 5 and shown in Fig. 2.

give identical energies. Some computations were made for the k cell also: the point of using all three cells is to provide a check on the calculations. The cells are all orthorhombic (rectangular boxes) with dimensions  $a, b, c$  given in terms of the oxygen–oxygen nearest-neighbour distance  $R$  as follows:

$a/R$	$b/R$	$c/R$	$b/a$	$c/a$	$abc/R^3$
h: $\sqrt{8/3}$	$\sqrt{8}$	$8/3$	$\sqrt{3}$	$\sqrt{8/3}$	$64/3\sqrt{3}$
j: $\sqrt{8}$	$\sqrt{8/3}$	$8/3$	$1/\sqrt{3}$	$\sqrt{8/3}$	$64/3\sqrt{3}$
k: $2\sqrt{8/3}$	$\sqrt{8}$	$8/3$	$\sqrt{3}/2$	$\sqrt{2/3}$	$128/3\sqrt{3}$

In each case we choose the origin on an oxygen in the lower corner of the cell. The  $x, y, z$  coordinates of the oxygen nuclei expressed in units of  $a, b, c$  for the appropriate cell (i.e.  $\xi, \eta, \zeta$  represents coordinates  $a\xi, b\eta, c\zeta$ ), are as follows:

h:	000	$\frac{1}{2}\frac{1}{2}0$	$00\frac{3}{8}$	$\frac{1}{2}\frac{1}{2}\frac{3}{8}$
	$0\frac{1}{3}\frac{1}{2}$	$\frac{1}{2}\frac{5}{6}\frac{1}{2}$	$0\frac{1}{3}\frac{7}{8}$	$\frac{1}{2}\frac{5}{6}\frac{7}{8}$
j:	000	$\frac{1}{2}\frac{1}{2}0$	$00\frac{3}{8}$	$\frac{1}{2}\frac{1}{2}\frac{3}{8}$
	$\frac{1}{3}0\frac{1}{2}$	$\frac{5}{6}\frac{1}{2}\frac{1}{2}$	$\frac{1}{3}0\frac{7}{8}$	$\frac{5}{6}\frac{1}{2}\frac{7}{8}$
k:	000	$\frac{1}{2}00$	$\frac{1}{4}\frac{1}{2}0$	$\frac{3}{4}\frac{1}{2}0$
	$00\frac{3}{8}$	$\frac{1}{2}0\frac{3}{8}$	$\frac{1}{4}\frac{1}{2}\frac{3}{8}$	$\frac{3}{4}\frac{1}{2}\frac{3}{8}$
	$0\frac{1}{3}\frac{1}{2}$	$\frac{1}{2}\frac{1}{3}\frac{1}{2}$	$\frac{1}{4}\frac{5}{6}\frac{1}{2}$	$\frac{3}{4}\frac{5}{6}\frac{1}{2}$
	$0\frac{1}{3}\frac{7}{8}$	$\frac{1}{2}\frac{1}{3}\frac{7}{8}$	$\frac{1}{4}\frac{5}{6}\frac{7}{8}$	$\frac{3}{4}\frac{5}{6}\frac{7}{8}$

It is interesting to compare the hexagonal and cubic lattices of ices Ih and Ic. In each case there are four nearest oxygen neighbours of a given oxygen, at distance  $R$ , and 12 second neighbours at distance  $\sqrt{8/3}R$ . The differences begin at the third neighbour: the cubic lattice has 12 third neighbours at  $\sqrt{11/3}R$ , while the hexagonal lattice has one third neighbour at  $(5/3)R$  and then nine third neighbours at  $\sqrt{11/3}R$ . The coordination numbers up to the nearest fourth neighbour (counting bonds) are given below:

Neighbour	(Distance/ <i>R</i> )	9(Distance/ <i>R</i> ) <sup>2</sup>	Cubic	Hexagonal
1	1	9	4	4
2	$\sqrt{8/3}$	24	12	12
3 <i>h</i>	5/3	25	—	1
3	$\sqrt{11/3}$	33	12	9
4	$4/\sqrt{3}$	48	3	3
3 <i>h</i> '	7/3	49	—	6
3'	$\sqrt{57/3}$	57	12	9

(3)

In both lattices each oxygen site is equivalent to any other (until the hydrogens are put into place) but in the hexagonal case the *c* direction (the optic axis, also the *z*-axis in our choice of coordinates) is special. The third neighbour at closest distance in the hexagonal lattice is directly above or below (in the *c* direction) any given oxygen nucleus. In cubic ice Ic the oxygens occupy the carbon sites in a diamond lattice, and all oxygen hexagons are in the “chair” configuration. In hexagonal ice Ih the hexagons formed by the oxygens are “chairs” in the basal plane (perpendicular to the optic axis), and “boats” in prism planes (parallel to the optic axis).

### 3. Oxygen–oxygen Coulomb energies

Each charge in the unit cell interacts with all the other charges in the cell, and also with the triply infinite set of images (periodic repetitions) of itself and of other charges in the unit cell. The author has developed formulae for the rapid evaluation of these electrostatics interactions for cubic unit cells [15], and recently for rhombohedral unit cells [16] following the methods of Sperb [17]. (Extension of the results of Ref. [15] to rhombohedral cells in quasi-two-dimensional systems has been given in Ref. [18].) The Coulomb energy per cell of the interaction of charges *q<sub>i</sub>* in a cell of dimensions *a, b, c* is

$$U = a^{-1} \sum_i \sum_{i < j} q_i q_j V_{ij}, \tag{4}$$

where *V<sub>ij</sub>* is short for the dimensionless potential *V(a, b, c; ξ<sub>ij</sub>, η<sub>ij</sub>, ζ<sub>ij</sub>)* with

$$\begin{aligned} \xi_{ij} &= (x_i - x_j)/a, & \eta_{ij} &= (y_i - y_j)/b, \\ \zeta_{ij} &= (z_i - z_j)/c. \end{aligned} \tag{5}$$

The potential function *V* is given by [16]

$$\begin{aligned} V(a, b, c; \xi, \eta, \zeta) &= 4 \sum_{l=1}^{\infty} \cos(2\pi l \xi) \sum_{m, n=-\infty}^{\infty} K_0(2\pi l \rho_{mn}(\eta, \zeta)) \\ &\quad - \sum_{n=-\infty}^{\infty} \log[1 - 2 \cos(2\pi \eta)] \\ &\quad \times \exp(-2\pi|\zeta + n|c/b) + \exp(-4\pi|\zeta + n|c/b) \\ &\quad + 2\pi \left(\frac{c}{b}\right) [\zeta^2 - |\zeta|] + C(a, b, c), \end{aligned} \tag{6}$$

where

$$\begin{aligned} \rho_{mn}^2(\eta, \zeta) &= \left(\frac{b}{a}\right)^2 (\eta + m)^2 + \left(\frac{c}{a}\right)^2 (\zeta + n)^2, \\ C(a, b, c) &= 2 \log(4\pi a/b) - 2\gamma \\ &\quad + 4 \sum_{n=1}^{\infty} \log[1 - \exp(-2\pi n c/b)] \\ &\quad - 4 \sum_{l=1}^{\infty} \sum_{m, n=-\infty}^{\infty} K_0(2\pi l [(bm)^2 + (cn)^2]^{1/2}/a). \end{aligned} \tag{7}$$

(The prime on the *m, n* summation means that the *m, n* = 0 term is to be omitted.)

Although the Coulomb energy per cell is defined only for neutral systems ( $\sum q_i = 0$ ), the energy of an ice lattice can be notionally split into oxygen–oxygen, oxygen–hydrogen and hydrogen–hydrogen interaction terms:

$$\begin{aligned} U &= a^{-1} \{ (2q)^2 V_{OO} - 2q^2 V_{OH} + q^2 V_{HH} \} \\ &= (q^2/a) \{ 4V_{OO} - 2V_{OH} + V_{HH} \}. \end{aligned} \tag{8}$$

For a unit cell with eight water molecules, for example,  $V_{\text{OO}}$  is the sum over 28 interactions between the eight oxygens in the cell,  $V_{\text{OH}}$  is the sum over 128 interactions between each oxygen and each hydrogen, and  $V_{\text{HH}}$  is the sum over 120 interactions between the hydrogens.

The split into three interaction types is convenient, but, as we shall see, only the total energy has meaning, and (for example) the value of  $V_{\text{OO}}$  per molecule may have different values in different cells. In the cubic unit cell of ice Ic, containing eight oxygens, the translational and cubic symmetries reduce the 28 interactions to two types, and [1]

$$V_{\text{OO}}^{\text{c}} = 16V(L, L, L; \frac{1}{4}, \frac{1}{4}, \frac{1}{4}) + 12V(L, L, L; 0, \frac{1}{2}, \frac{1}{2}), \quad (9)$$

where  $L = 4R/\sqrt{3}$ . (Note that the cubic cell has the same volume as the *h* and *j* cells.) The Coulomb energy of oxygen–oxygen interactions per HOH unit is [1]

$$u_{\text{OO}}^{\text{c}} = \frac{4q^2}{L} V_{\text{OO}}^{\text{c}}/8 \approx 14.992270q^2/R. \quad (10)$$

For the *h* cell of hexagonal ice Ih, writing  $V(\xi, \eta, \zeta)$  for  $V(a, b, c; \xi, \eta, \zeta)$ , where  $a, b, c$  are given in Eq. (1), we find

$$V_{\text{OO}}^{\text{h}} = 4\{V(0, 0, \frac{3}{8}) + V(0, \frac{1}{3}, \frac{1}{8}) + V(0, \frac{1}{3}, \frac{1}{2}) + V(\frac{1}{2}, \frac{1}{6}, \frac{1}{8}) + V(\frac{1}{2}, \frac{1}{6}, \frac{1}{2}) + V(\frac{1}{2}, \frac{1}{2}, 0) + V(\frac{1}{2}, \frac{1}{2}, \frac{3}{8})\}. \quad (11)$$

The oxygen–oxygen electrostatic interactions, per HOH unit, evaluate to

$$u_{\text{OO}}^{\text{h}} = \frac{4q^2}{a_{\text{h}}} V_{\text{OO}}^{\text{h}}/8 \approx 13.083776q^2/R. \quad (12)$$

For the *j* cell of Ih, again omitting  $a, b$  and  $c$  from the potential, the oxygen–oxygen interactions reduce to

$$V_{\text{OO}}^{\text{j}} = 4\{V(0, 0, \frac{3}{8}) + V(\frac{1}{6}, \frac{1}{2}, \frac{1}{8}) + V(\frac{1}{6}, \frac{1}{2}, \frac{1}{2}) + V(\frac{1}{3}, 0, \frac{1}{8}) + V(\frac{1}{3}, 0, \frac{1}{2}) + V(\frac{1}{2}, \frac{1}{2}, 0) + V(\frac{1}{2}, \frac{1}{2}, \frac{3}{8})\}. \quad (13)$$

The electrostatic energy per water molecule is likewise

$$u_{\text{OO}}^{\text{j}} = \frac{4q^2}{a_{\text{j}}} V_{\text{OO}}^{\text{j}}/8 \approx 13.083766q^2/R. \quad (14)$$

Finally, for the 16-molecule Kamb cell, the 120 oxygen–oxygen interactions fall into 11 classes

$$V_{\text{OO}}^{\text{k}} = 8\{V(0, 0, \frac{3}{8}) + V(0, \frac{1}{3}, \frac{1}{8}) + V(0, \frac{1}{3}, \frac{1}{2}) + 2[V(\frac{1}{4}, \frac{1}{6}, \frac{1}{8}) + V(\frac{1}{4}, \frac{1}{6}, \frac{1}{2}) + V(\frac{1}{4}, \frac{1}{2}, 0) + V(\frac{1}{4}, \frac{1}{2}, \frac{3}{8})] + V(\frac{1}{2}, 0, 0) + V(\frac{1}{2}, 0, \frac{3}{8}) + V(\frac{1}{2}, \frac{1}{3}, \frac{1}{8}) + V(\frac{1}{2}, \frac{1}{3}, \frac{1}{2})\}. \quad (15)$$

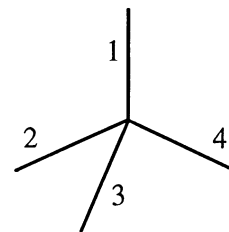
The O–O Coulomb energy per HOH unit is

$$u_{\text{OO}}^{\text{k}} = \frac{4q^2}{a_{\text{k}}} V_{\text{OO}}^{\text{k}}/16 \approx 26.194596q^2/R. \quad (16)$$

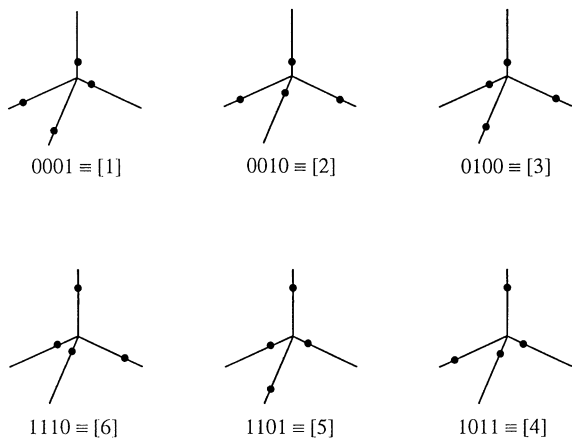
We see that the oxygen–oxygen interaction (per water molecule) is different in the *k* cell from what it is in the *h* and *j* cells. Of course, the total energy per molecule is the same for the same proton arrangements, irrespective of the cell used for the calculation. To see that the partial terms can be very different, consider an ionic lattice of the CsCl type. For a cell with just one plus and one minus ion, there is only the (+ –) interaction within the cell. For a cell with two plus and two minus ions, there are (+ +) and (– –) interactions, as well as two (+ –) interactions. See Section 4 of Ref. [16], where use is made of the equality of the total energy per charge pair.

#### 4. Allowed hydrogen configurations, and their classification

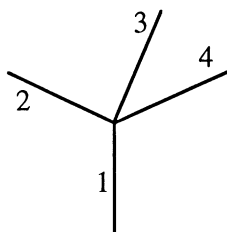
As in the case of cubic ice Ic [1], we wish to enumerate the proton arrangements in each cell which are in accord with the “ice rules” [9] (two protons near each oxygen, one proton on each O–O bond). Consider the four hydrogens on bonds emanating from one oxygen, at the vertex of the figure



We represent up and down positions by 1 and 0. Then, as is well known [2–4], six of the 16 arrangements are allowed, namely,



The protons around each oxygen must be in one of the allowed configurations. (For the inverted bond structure, namely



the same numberings give the allowed positions.) Each of the above allowed arrangements can be interpreted as a binary number, and each of these has a decimal equivalent:

[1]	[2]	[3]	[4]	[5]	[6]
0001	0010	0100	1011	1101	1110
1	2	4	11	13	14

(17)

This enables us to program a computer search for the allowed configurations. Fig. 1 shows the numbering of the protons in the h (half-Kamb) cell. The peculiar numbering is chosen so as to make each row of the array

1	2	3	4
5	6	7	8
9	10	11	12
13	14	15	16

(18)

be constrained by the ice rules to be a member of the set (17). In addition, the following four proton quartets must be members of (17):

$$(1, 10, 12, 14) \quad (5, 11, 15, 16) \quad (13, 2, 6, 7) \quad (9, 3, 4, 8). \quad (19)$$

Note that there are eight constraints in all, one for each oxygen atom in the cell, and that these eight constraints have incorporated the periodic boundary conditions on the ice superlattice made up of this unit cell.

There are 114 possible proton arrangements in a superlattice made of h cells (and the same number in a superlattice made up of j cells, of course). This is somewhat larger than the 90 hydrogen configurations in the cubic cell made up of the same number (eight) of HOH units. In the cubic 8-molecule cell the symmetries reduced the number of energetically distinct configurations from 90 to 4 (all of the possible proton arrangements were shown to lead to the same Coulomb energy  $V_{OH}$ , so the differences were within  $V_{HH}$ ). For all the unit cells in hexagonal ice Ih we again find that the electrostatic oxygen–hydrogen interactions are invariant with respect to the hydrogen arrangements. For the h and j eight-molecule unit cells, we find that there are 17 different H–H potential functions among the 114 allowed proton configurations, of which ([1 3 2 3], [1 3 3 1]) and ([1 3 1 2], [3 1 2 3]) are degenerate, leaving 15 distinct energies. As in the case of cubic ice Ic, the lowest state, namely [1 4 4 1], is antiferroelectric.

### 5. Cell dipole moments and H–H energies

In cubic ice Ic we found that there was a simple linear relation between the energy of a proton configuration and the square of the cell dipole moment. We will attempt to correlate the energies of hexagonal ice Ih in the same way. To this end, we need to define the dipole moments in terms of the proton

coordinates. We will choose a definition such that the dipole moment of the cell is zero when all the hydrogens are positioned midway between the oxygens ( $f = \frac{1}{2}$ ).

The following applies to the h cell, with oxygen and proton numberings as in Fig. 1. Of the oxygens, 4, 6 and 8 are internal to the cell, 2, 5 and 7 are on a face (shared between two cells), 3 is on an edge (shared between four cells), and 1 is at a corner (shared between eight cells). The centre of mass of the oxygens is at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) + (0, \frac{1}{24}, \frac{1}{16})$ , where the entries stand for  $(x/a, y/b, z/c)$ .

Of the protons, 1 is on an edge, 2, 13 and 14 are on a face, and the others are internal to the cell. When  $f = \frac{1}{2}$  their centre of mass is at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) + (0, \frac{7}{96}, \frac{1}{8})$ . The combined  $f = \frac{1}{2}$  dipole moment is thus, in units of  $q(a, b, c)$ ,

$$-16(0, \frac{1}{24}, \frac{1}{16}) + 16(0, \frac{7}{96}, \frac{1}{8}) = (0, \frac{1}{2}, 1). \quad (20)$$

Let  $\mathbf{d}_i$  and  $\mathbf{u}_i$  represent the positions of the oxygens below and above proton  $i$ . From Eq. (4) of Ref. [1], the position of proton  $i$  is

$$\mathbf{r}_i = (1 - f)\mathbf{d}_i + f\mathbf{u}_i + (1 - 2f)b_i(\mathbf{u}_i - \mathbf{d}_i), \quad (21)$$

where  $b_i$  is 1 when the proton is up and 0 when the proton is down (on the bond joining the oxygens at  $\mathbf{d}_i$  and  $\mathbf{u}_i$ ). In view of the fact that protons 1, 2, 13 and 14 are shared with other cells, the vectors  $\mathbf{u}_i$  and  $\mathbf{d}_i$  should be modified as follows for the computation of dipole moments:

$$\begin{aligned} \mathbf{d}_1, \mathbf{u}_1: & \text{add } (\frac{1}{2}, \frac{1}{2}, 0), \\ \mathbf{d}_2, \mathbf{u}_2, \mathbf{d}_{13}, \mathbf{u}_{13}, \mathbf{d}_{14}, \mathbf{u}_{14}: & \text{add } (\frac{1}{2}, 0, 0). \end{aligned} \quad (22)$$

With these modifications, and subtraction of the  $f = \frac{1}{2}$  dipole moment (20), the net cell moment relative to the  $f = \frac{1}{2}$  value is

$$\mathbf{D} = (1 - 2f)\{\sum b_i(\mathbf{u}_i - \mathbf{d}_i) - (0, 0, \frac{3}{2})\}, \quad (23)$$

again in units of  $q(a, b, c)$ . For example, for the lowest energy antiferroelectric configuration [1441], the binary numbers  $b_i$  are given in the array

$$\begin{array}{cccc} 0 & 0 & 0 & 1 \\ 1 & 0 & 1 & 1 \\ 1 & 0 & 1 & 1 \\ 0 & 0 & 0 & 1 \end{array} \quad (24)$$

so  $b_4, b_5, b_7, b_8, b_9, b_{11}, b_{12}, b_{16}$  are unity, the others being zero. The result obtained from Eq. (23) is then  $\mathbf{D}[1441] = (0, 0, 0)$ . The ferroelectric configuration (with only four of 16 protons up),

$$[1211] \equiv \begin{array}{cccc} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 \end{array} \quad (25)$$

has the dipole moment

$$\mathbf{D}[1211] = q(1 - 2f)(0, 0, -c) \quad (26)$$

which we represent as  $(0, 0, -1)$ . Finally, the two ferroelectric configurations of highest energy, namely,

$$\begin{aligned} [1323] & \equiv \begin{array}{cccc} 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{array} \\ [1331] & \equiv \begin{array}{cccc} 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{array} \end{aligned} \quad (27)$$

have dipoles  $(1, 1, -1)$  and  $(2, 0, -1)$ . Since for the h cell

$$a = \sqrt{8/3}R, \quad b = \sqrt{8}R, \quad c = (8/3)R, \quad (28)$$

these two dipoles have the same square, namely  $(160/9)(1 - 2f)^2(qR)^2$ .

The 17 distinct proton configurations, with their H–H energies calculated at  $f = 0.35$ , and their dipole moments, are given in Table 1. The energies are given relative to the lowest, namely [1441], which has a H–H Coulomb interaction per molecule of  $15.207640q^2/R$  (all energy values have been rounded to the sixth decimal place, and are coefficients of  $q^2/R$ ).

The first column gives the configuration type, the second the number of configurations of this type (these add to 114), the third the dipole, with  $(\alpha, \beta, \gamma)$  representing dipole  $q(1 - 2f)(\alpha a, \beta b, \gamma c)$ . The  $(\text{dipole})^2$  value is the coefficient of  $\frac{1}{3}(1 - 2f)^2(qR)^2$

Table 1

Type	Number	Dipole	(Dipole) <sup>2</sup>	Energy
[1323]	8	(11 $\bar{1}$ )	160	0.005829
[1331]	4	(20 $\bar{1}$ )	160	0.005829
[1223]	8	(011)	136	0.005067
[1625]	8	(110)	96	0.004405
[1626]	8	(010)	72	0.004359
[1232]	4	(00 $\bar{1}$ )	64	0.004213
[1212]	16	( $\bar{1}$ 0 $\bar{1}$ )	88	0.004212
[1312]	4	(00 $\bar{1}$ )	64	0.004120
[3123]	2	(00 $\bar{1}$ )	64	0.004120
[1634]	8	(100)	24	0.003503
[1561]	4	(200)	96	0.003143
[1614]	8	(000)	0	0.002694
[1211]	4	(00 $\bar{1}$ )	64	0.002686
[1462]	4	(000)	0	0.001527
[1442]	16	( $\bar{1}$ 00)	24	0.001525
[1542]	4	(000)	0	0.001432
[1441]	4	(000)	0	0

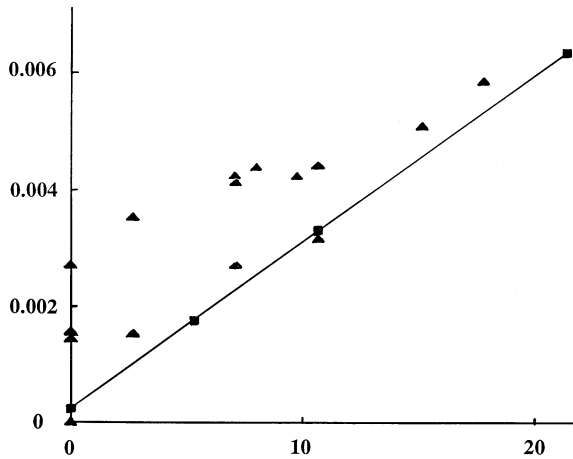


Fig. 2. The 15 different energies of the 114 allowed proton configurations in the h cell of hexagonal ice Ih (triangles), shown together with the four different energies of 90 allowed configurations of an eight-molecule cell of cubic ice Ic (squares). The horizontal coordinate is the coefficient of  $(1 - 2f)^2(qR)^2$  in the square of the dipole moment per cell. The vertical coordinate is the coefficient of  $q^2/R$  in  $E - E_0$  evaluated at  $f = 0.35$ ,  $E_0$  being the energy of the lowest configuration in Ih, namely [1441].

in the expression for the square of the dipole moment. The [1323], [1331] and [1312], [3123] entries are believed to degenerate (i.e. of identical energy for all  $f$ ); the symmetry underlying these identities is not yet understood.

Fig. 2 shows the  $f = 0.35$  energies versus the coefficient of  $(1 - 2f)^2(qR)^2$  in the square of the dipole moment, for 8-molecule cells of cubic ice Ic [1] as well as for the hexagonal ice Ih under consideration here. We see that the energy of a configuration is correlated with the square of the cell dipole moment, but not perfectly, as was the case in cubic ice Ic. It seems that in the cubic structure the  $x, y, z$  symmetry allows the Coulomb energy differences to be represented by the interaction of pure dipoles, distributed within each cell. The hexagonal case is more complicated, and so higher moments than just the dipole must be used to represent cell–cell interactions. For example, four configuration types have zero-dipole moment, but their energies are not the same.

### 6. Total energies, and comparison of hexagonal and cubic ices

We first comment on the sensitivity of the component energies to  $f = r/R$ . The oxygen–oxygen Coulomb interactions are independent of  $f$ , of course; these have been given in Eqs. (12), (14) and (16).

There is only one oxygen–hydrogen interaction energy, irrespective of the proton configuration, just as was the case in cubic ice Ic (see Ref. [1], especially the appendix). It is interesting that “illegal” configurations, which have (correctly) one hydrogen on each O–O bond but have fewer or more than the correct number of two hydrogens next to each oxygen, also have the same O–H Coulomb energy, namely,

$$\begin{aligned}
 V_{\text{OH}}^{\text{h}} = & 4V\left(0, 0, \frac{3f}{8}\right) + 4V\left(0, 0, \frac{3}{8} - \frac{3f}{8}\right) \\
 & + 4V\left(0, \frac{1}{3} - \frac{f}{3}, \frac{1}{8} - \frac{f}{8}\right) + 4V\left(0, \frac{1}{3} - \frac{f}{3}, \frac{1}{2} - \frac{f}{8}\right) \\
 & + 4V\left(0, \frac{f}{3}, \frac{f}{8}\right) + 4V\left(0, \frac{1}{3}, \frac{1}{8} + \frac{3f}{8}\right) \\
 & + 4V\left(0, \frac{1}{3}, \frac{1}{2} - \frac{3f}{8}\right) + 4V\left(0, \frac{1}{3}, \frac{3}{8} + \frac{f}{8}\right) \\
 & + 8V\left(\frac{f}{2}, \frac{f}{6}, \frac{f}{8}\right) + 8V\left(\frac{f}{2}, \frac{f}{6}, \frac{3}{8} + \frac{f}{8}\right)
 \end{aligned}$$

$$\begin{aligned}
& + 8V\left(\frac{f}{2}, \frac{1}{3} + \frac{f}{6}, \frac{1}{8} - \frac{f}{8}\right) \\
& + 8V\left(\frac{f}{2}, \frac{1}{3} + \frac{f}{6}, \frac{1}{2} - \frac{f}{8}\right) \\
& + 8V\left(\frac{1}{2} - \frac{f}{2}, \frac{1}{6} - \frac{f}{6}, \frac{1}{8} - \frac{f}{8}\right) \\
& + 8V\left(\frac{1}{2} - \frac{f}{2}, \frac{1}{6} - \frac{f}{6}, \frac{1}{2} - \frac{f}{8}\right) \\
& + 8V\left(\frac{1}{2} - \frac{f}{2}, \frac{1}{2} - \frac{f}{6}, \frac{f}{8}\right) \\
& + 8V\left(\frac{1}{2} - \frac{f}{2}, \frac{1}{2} - \frac{f}{6}, \frac{3}{8} + \frac{f}{8}\right) \\
& + 4V\left(\frac{1}{2}, \frac{1}{6}, \frac{1}{8} + \frac{3f}{8}\right) + 4V\left(\frac{1}{2}, \frac{1}{6}, \frac{1}{2} - \frac{3f}{8}\right) \\
& + 4V\left(\frac{1}{2}, \frac{1}{6} + \frac{f}{3}, \frac{1}{8} - \frac{f}{8}\right) + 4V\left(\frac{1}{2}, \frac{1}{6} + \frac{f}{3}, \frac{1}{2} - \frac{f}{8}\right) \\
& + 4V\left(\frac{1}{2}, \frac{1}{2} - \frac{f}{3}, \frac{f}{8}\right) + 4V\left(\frac{1}{2}, \frac{1}{2} - \frac{f}{3}, \frac{3}{8} + \frac{f}{8}\right) \\
& + 4V\left(\frac{1}{2}, \frac{1}{2}, \frac{3f}{8}\right) + 4V\left(\frac{1}{2}, \frac{1}{2}, \frac{3}{8} - \frac{3f}{8}\right). \quad (29)
\end{aligned}$$

The above expression is for the h cell, with  $V(\xi, \eta, \zeta)$  short for  $V(a, b, c; \xi, \eta, \zeta)$ . The 128 interactions are of 24 types. The variation of  $V_{\text{OH}}^{\text{h}}$  with  $f$  is similar to that for cubic ice, shown in Fig. 2 of Ref. [1]. Two particular values of  $u_{\text{OH}}^{\text{h}}$  (the Coulomb oxygen–hydrogen interaction energy, per molecule) are

$$\begin{aligned}
f = 0.35 & & f = 0.5 \\
-38.700564q^2/R & & -36.998626q^2/R
\end{aligned} \quad (30)$$

The 114 possible proton configurations in the h or j cells lead to 17 distinct potential functions, with two pairwise degeneracies, as we saw in the last section. The lowest energy is obtained by the zero-dipole antiferroelectric configuration [1441], at all values of  $f$ . For the h cell this has the

form

$$\begin{aligned}
V_{\text{HH}}^{\text{h}}[1441] = & 4V\left(0, \frac{f}{3}, \frac{3}{8} - \frac{f}{4}\right) + 2V\left(0, \frac{1}{3} - \frac{2f}{3}, \frac{1}{2}\right) \\
& + 4V\left(0, \frac{1}{3} - \frac{f}{3}, \frac{1}{8} + \frac{f}{4}\right) + 2V\left(0, \frac{1}{3}, \frac{1}{2}\right) \\
& + 4V\left(0, \frac{1}{3} + \frac{f}{3}, \frac{1}{2}\right) + 4V\left(\frac{f}{2}, \frac{1}{3} - \frac{f}{6}, \frac{1}{8} - \frac{f}{4}\right) \\
& + 4V\left(\frac{f}{2}, \frac{f}{6}, \frac{f}{2}\right) + 4V\left(\frac{f}{2}, \frac{1}{3} + \frac{f}{6}, \frac{1}{8} + \frac{f}{4}\right) \\
& + 4V\left(\frac{f}{2}, \frac{1}{3} + \frac{f}{6}, \frac{1}{2} - \frac{f}{2}\right) + 4V\left(\frac{f}{2}, \frac{1}{3} - \frac{f}{2}, \frac{f}{2}\right) \\
& + 4V\left(\frac{f}{2}, \frac{f}{2}, 0\right) + 4V\left(\frac{f}{2}, \frac{f}{6}, \frac{3}{8} - \frac{f}{4}\right) \\
& + 4V\left(\frac{f}{2}, \frac{f}{2}, \frac{3}{8} + \frac{f}{4}\right) + 4V\left(f, \frac{1}{3} + \frac{f}{3}, \frac{1}{8} - \frac{f}{4}\right) \\
& + 4V\left(f, 0, \frac{3}{8} + \frac{f}{2}\right) + 4V\left(\frac{1}{2} - f, \frac{1}{2}, 0\right) \\
& + 4V\left(\frac{1}{2} - f, \frac{1}{6} - \frac{f}{3}, \frac{1}{2}\right) \\
& + 4V\left(\frac{1}{2} - \frac{f}{2}, \frac{1}{6} - \frac{f}{6}, \frac{1}{8} + \frac{f}{4}\right) \\
& + 4V\left(\frac{1}{2} - \frac{f}{2}, \frac{1}{2} - \frac{f}{2}, 0\right) \\
& + 4V\left(\frac{1}{2} - \frac{f}{2}, \frac{1}{2} - \frac{f}{6}, \frac{3}{8} - \frac{f}{4}\right) \\
& + 4V\left(\frac{1}{2} - \frac{f}{2}, \frac{1}{2} - \frac{f}{6}, \frac{f}{2}\right) \\
& + 4V\left(\frac{1}{2} - \frac{f}{2}, \frac{1}{6} - \frac{f}{6}, \frac{1}{2} - \frac{f}{2}\right) \\
& + 4V\left(\frac{1}{2} - \frac{f}{2}, \frac{1}{6} - \frac{f}{6}, \frac{1}{8} - \frac{f}{4}\right)
\end{aligned}$$



$$\begin{aligned}
 &+ 4V\left(\frac{1}{2} - \frac{f}{2}, \frac{1}{2} - \frac{f}{2}, \frac{3}{8} + \frac{f}{2}\right) \\
 &+ 4V\left(\frac{1}{2} - \frac{f}{2}, \frac{1}{6} + \frac{f}{6}, \frac{1}{2}\right) + 4V\left(\frac{1}{2}, \frac{1}{2}, 0\right) \\
 &+ 4V\left(\frac{1}{2}, \frac{1}{6}, \frac{1}{2}\right) + 4V\left(\frac{1}{2}, \frac{1}{2} - \frac{f}{3}, \frac{3}{8} - \frac{f}{4}\right) \\
 &+ 4V\left(\frac{1}{2}, \frac{1}{6} - \frac{f}{3}, \frac{1}{8} - \frac{f}{4}\right) \\
 &+ 2V\left(\frac{1}{2}, \frac{1}{6} + \frac{2f}{3}, \frac{1}{2}\right) + 4V\left(\frac{1}{2}, \frac{1}{6} + \frac{f}{3}, \frac{1}{8} + \frac{f}{4}\right) \\
 &+ 4V\left(\frac{1}{2}, \frac{1}{2}, \frac{3}{8} + \frac{f}{4}\right). \tag{31}
 \end{aligned}$$

The 120 interactions are of 32 types. The variation of  $u_{\text{HH}}$  with  $f$  is similar to that for cubic ice (Fig. 2 of Ref. [1]). Two particular values of  $u_{\text{HH}}^{\text{h}}$  are

$$\begin{aligned}
 f = 0.35 \quad [1\ 4\ 4\ 1] & \quad f = 0.5 \quad [\text{all configurations}] \\
 15.207640q^2/R & \quad 15.008273q^2/R. \tag{32}
 \end{aligned}$$

At  $f = 0$  and  $\frac{1}{2}$  all the proton configurations are equivalent; for intermediate  $f$  the  $[1\ 4\ 4\ 1]$  configuration is the lowest in energy. Fig. 3 shows the differences  $\Delta u_{\text{HH}}^{\text{h}} = u_{\text{HH}}^{\text{h}} - u_{\text{HH}}^{\text{h}} [1\ 4\ 4\ 1]$  for four configurations. To high accuracy, they all fit a curve of the form

$$\Delta u = g^2\left(\frac{1}{2} - f\right)^2(c_0 + c_1^3g + c_2g^2 + c_3g^3)q^2/R, \tag{33}$$

where  $g = f(1 - f)$ .

Thus, the antiferroelectric configuration has the lowest energy, just as we found for cubic ice [1]. This is in agreement with a recent simulation [13], but not with theoretical predictions [19,20].

Finally, we compare the hexagonal and cubic forms of ice I. The differences between the highest and lowest energies of the possible hydrogen configurations are similar: at  $f = 0.35$  these are

$$\begin{aligned}
 \text{hexagonal} & \quad \text{cubic} \\
 0.005829q^2/R & \quad 0.006088q^2/R. \tag{34}
 \end{aligned}$$

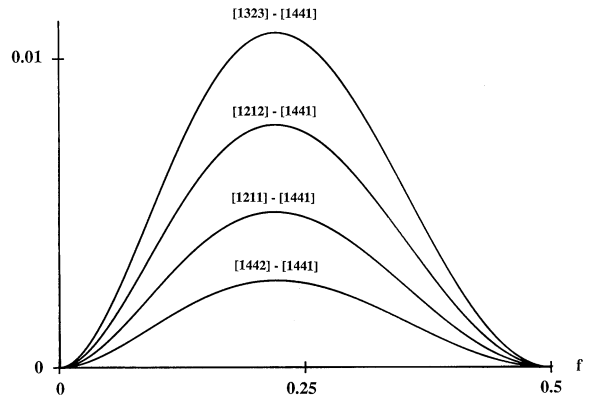


Fig. 3. Energies of four configurations relative to the lowest energy configuration  $[1\ 4\ 4\ 1]$ , as a function of  $f = r/R$  (the ratio of the hydrogen–oxygen closest distance  $r$  to the oxygen–oxygen near neighbour distance  $R$ ). The vertical coordinate is the coefficient of  $q^2/R$  in  $\Delta u$ .

The total energies per molecule of the configurations of lowest energy in Ih and Ic are (again at  $f = 0.35$ )

$$\begin{aligned}
 \text{hexagonal } [1\ 4\ 4\ 1] & \quad \text{cubic } [3\ 2\ 2\ 3] \\
 - 10.409148q^2/R & \quad - 10.408909q^2/R. \tag{35}
 \end{aligned}$$

We see that the Coulomb energy per molecule is lower in the naturally dominant form of ice, by about  $0.000\ 239q^2/R$ . For  $q = 0.5|e|$  and  $R = 2.75\text{\AA}$ ,  $q^2/R \approx 1.309\text{ eV}$ , so the energy advantage of hexagonal over cubic ice is about  $0.3\text{ meV}$  per molecule. Even the largest charge on the hydrogens which has been proposed (namely,  $0.865|e|$  [13]), would give an energy difference smaller than the measured heat release of  $8.8\text{ J/g}$ , or  $1.65\text{ meV}$  per molecule, when Ic converts to Ih between  $-113^\circ\text{C}$  and  $-63^\circ\text{C}$  (Ref. [3], p. 57). We conclude that our results are consistent with Nature’s preference for hexagonal ice over cubic ice, but note that this conclusion rests on the assumption of identical chemical bonding and nearest-neighbour distances in the two lattices, and has taken no account of entropic considerations. A more robust deduction from our results is that electrostatics favours the antiferroelectric arrangements, in both hexagonal and cubic ices.

## Appendix A. Electrostatics of diamond

Diamond is tetrahedrally bonded, like the low-pressure ices, and correspondingly both cubic and hexagonal forms may be expected to exist. In the case of diamond (and also for silicon and germanium) the preferred lattice is cubic, but hexagonal diamond has been found in some meteorites, and has been made in the laboratory [21–24]. Diamond bonds covalently (by the sharing of electrons). The carbon nuclei are not completely shielded by their electrons, which are distributed also along the carbon–carbon bonds. There is thus a net charge  $2q$  centred on each carbon nucleus, and a charge  $-q$  distributed on each bond. There is no reason to suppose that the electron charge on the bonds is asymmetric with respect to the point midway between the neighbour carbon nuclei. Thus, the simplest model for the electrostatics of diamond is analogous to the ice model used here, with the charges  $-q$  centred on each bond, i.e. with  $f = r/R = \frac{1}{2}$ . The electrostatic energies per atom are then, calculated at  $f = \frac{1}{2}$  by the methods of this paper and of [1],

$$\begin{array}{ll} \text{hexagonal} & \text{cubic} \\ -8.906577q^2/R & -8.906753q^2/R. \end{array} \quad (36)$$

The cubic lattice thus has the lower electrostatic energy, by about  $0.000176q^2/R$  per carbon atom. With  $R = 1.5445 \text{ \AA}$  [24] and an assumed  $q$  value of one half  $|e|$ ,  $q^2/R \approx 2.33 \text{ eV}$ , and the Coulomb energy difference is about  $0.41 \text{ meV}$  per atom, or  $40 \text{ J/g}$ .

The covalent electrons are spread out along the bond, not concentrated in the middle, so these numbers must, of course, be treated as just rough estimates for the electrostatic energies. In addition, there is a possible difference between the bonding energies in the chair and boat configurations of carbon hexagons. Nevertheless, the numbers do indicate one reason why cubic diamond is the form most frequently found.

Fig. 4 shows the difference between the Coulomb energies of the cubic and hexagonal lattices, with charges of  $\pm 2q$  at the lattice points and  $\mp q$  at fraction  $f = r/R$  along the bonds between lattice sites. For  $f \neq \frac{1}{2}$  the lowest (antiferroelectric) config-

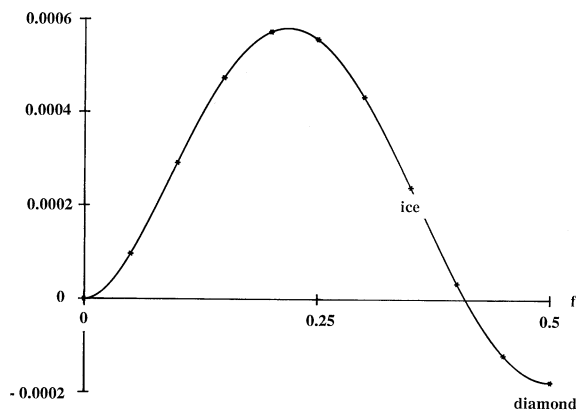


Fig. 4. The difference between the electrostatic energies of cubic and hexagonal tetrahedrally-bonded lattices. Charges  $2q$  are on lattice sites, and  $-q$  at fraction  $f$  along the bonds. For  $f \neq \frac{1}{2}$  we compare the energetically lowest configuration for each lattice. The ordinate is the coefficient of  $q^2/R$  in  $E_c - E_h$ . The curve is the function  $g^2(a + bg + cg^2 + dg^3 + eg^4)$ , where  $g = f(1 - f)$ , fitted to five of the calculated points shown.

urations are compared, as in Section 6. The ordinate times  $q^2/R$  gives the energy difference per lattice vertex. Ice at  $f \approx 0.35$  and diamond at  $f = \frac{1}{2}$  are indicated. We see that the hexagonal energy is lower for  $f \leq 0.409$ , and then the cubic energy becomes lower. Ice and diamond are on opposite sides of this point of electrostatic energy equality.

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