

Theory of Ice Structures

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The structures of nine phases of ice are described as the result of ordering and displacive mechanisms from a common parent disordered body centered cubic structure possessing different fractional concentrations of water molecules.

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Since the pioneering diffraction works of Tamman [1], Bridgmann [2,3], König [4], and more recently Kamb [5], Whalley [6], and some others [6–8], most of the structures of ice are well established. However, this information does not give any insight about the molecular steps of reorganization from one structure to another. Although a number of crystallographic models were proposed to connect some of the phases of ice [8], there has been no attempt, in the framework of the current theories of phase transitions, to describe comprehensively their structural relationships. This is due on the one hand to the extreme complexity of the phase diagram of ice, which contains not less than twelve stable or metastable phases, and on the other hand to the presupposed opinion that, as the transformations between the phases are of the reconstructive type, their mechanisms cannot be conveniently accounted by a standard phenomenological or microscopic scheme. The aim of the present work is to show, on the contrary, that at least nine of the ice structures can be understood within the same unified approach, which was recently proposed by the authors of this Letter for the fcc-hcp and graphite-diamond transitions [9]. More precisely, we will describe the phases of ice as the result of ordering and displacive mechanisms from a single parent disordered body centered cubic structure possessing different fractional concentrations of water molecules.

Let us first consider the normal hexagonal I_h (ice I) phase, which is found in the natural environment. The oxygen framework of its tridymite-type structure (space group $D_{6h}^4, Z=4$) is represented in Fig. 1(a). It consists of puckered hexagonal layers of water molecules forming hexagonal rings [10]. The four oxygen atoms contained in one unit cell are in crystallographic positions $4f$, the tetrahedral coordination of each molecule shifting the oxygen atoms with respect to the average positions of the layers along z in two opposite directions by $C_h/16$, where C_h is the hexagonal lattice vector. In Fig. 1(a) a substructure of I_h corresponding to a bcc structure (space group O_h^2) is indicated by dashed lines. Its unit cell is filled by $\frac{2}{3}$ water molecule; i.e., the oxygen atoms are randomly distributed among the sites. We will use this disordered structure, denoted hereafter I_o , to describe the formation of ice I_h as the result of a virtual I_o to I_h phase transformation. Furthermore, in this paper I_o will be

shown to be the maximal substructure common to all ice structures provided different concentrations of water molecules are used, and accordingly will be taken as the common parent phase for describing the formation of all the considered ice phases.

The mechanism transforming I_o into I_h can be described in two correlated steps, which are illustrated in Fig. 1(a): an ordering of the oxygen atoms which fill the $4f$ positions, with vacancies in $2a$ positions, and an antiparallel displacement of two pairs of atoms by $5C_h/48$ and $11C_h/48$, which is shown in Fig. 1(b) within the

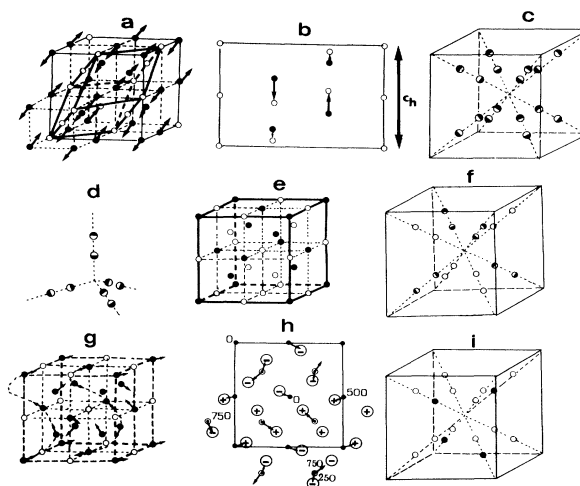


FIG. 1. Ordering and shifting mechanisms transforming the I_o bcc structure into ice I_h , ice I_c , and ice III. Full and open circles are, respectively, occupied and vacant atomic positions. Half-filled circles correspond to an occupancy $\frac{1}{2}$ of the sites. (a) Oxygens in the unit cells of I_o (small cubes) and I_h (thick lines). Long and short arrows are the two types of antiparallel shifts of the oxygens along C_h . (b) Projection of the preceding shifts within the (011) bcc plane. (c), (d) are the hydrogen distributions around oxygen sites within the I_o and I_h structures, respectively. (e) Oxygen frameworks for the I_o (small cubes) and I_c (large cube) structures. (f) Occupancy of the hydrogens in the I_c and ice VII structures. (g), (h) Shifting of the oxygens from I_o to ice III and their projection in the (000) bcc planes: the signs + and - correspond to the directions of the shifts along z . The numbers in (h) indicate the level of the atoms with respect to the basic plane. (i) Hydrogen distribution in the ice III and ice IX unit cells.

(011) bcc plane. Figures 1(c) and 1(d) give the corresponding distribution of hydrogen atoms within the I_o and I_h unit cells, in which they occupy respectively the positions $16f$ and $12k+4f$ with a probability of occupancy $\frac{1}{6}$ and $\frac{1}{2}$, respectively. The preceding coupled mechanism is accompanied by a large decompression of about 27% along the sixfold hexagonal axis.

In the group-theoretical formalism, the ordering and shifting of the oxygens, which constitute the primary transformation mechanism, is associated with a single eight-dimensional irreducible representation (IR) of the parent O_h^9 space group, denoted $\tau_1(\mathbf{k}_7)$ in Kovalev's notations [11]. In terms of the reciprocal bcc lattice vectors $\mathbf{k}_7 = \frac{1}{6}(\mathbf{a}_1^* + \mathbf{a}_2^* + \mathbf{a}_3^*)$. It corresponds in the direct space to the following relationship between the I_h and I_o unit-cell basic vectors: $\mathbf{a}_h = \mathbf{a}_1 - \mathbf{a}_2$, $\mathbf{b}_h = \mathbf{a}_2 - \mathbf{a}_3$, and $\mathbf{c}_h = 2(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)$.

Let us now show that the formation of the I_c structure of ice, which is stable at very low pressures and low temperatures, can be understood as the result of an analogous ordering process from the I_o structure. Figure 1(e) indicates by the dashed line the I_o unit cell within the cubic crystalite-type structure of I_c (space group $O_h^7, Z=2$) [12]. The three axes spanning the bcc primitive unit cell coincide with the axes of the conventional fcc unit cell of I_c , with a doubling of the three corresponding lattice parameters. The relationship between the primitive cubic lattice parameters of the I_c and I_o unit cells is $\mathbf{a}_c = 2\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3$, $\mathbf{b}_c = \mathbf{a}_1 + 2\mathbf{a}_2 + \mathbf{a}_3$, $\mathbf{c}_c = \mathbf{a}_1 + 2\mathbf{a}_3$. Thus the number of water molecules per unit cell in I_o is $\frac{1}{2}$. The molecules occupy in I_c the $2a$ crystallographic positions, the vacancies filling the positions $2b$. The hydrogens occupy the positions $8e$ and their distribution is given in Fig. 1(f). As the symmetries of I_o and I_c are related by a group-subgroup relationship, the $I_o \rightarrow I_c$ ordering transformation is described by a standard Landau-type approach: It is induced by the two-dimensional IR, denoted $\tau_1(\mathbf{k}_{10})$ of the O_h^9 space group, at the P point [$\mathbf{k}_{10} = \frac{1}{4}(\mathbf{a}_1^* + \mathbf{a}_2^* - \mathbf{a}_3^*)$] of the bcc Brillouin-zone surface [11].

Ice III, which is made from ice I_h by raising the pressure to above 2070 bars below -22°C , has a tetragonal structure [13] ($D_4^4, Z=12$) usually described from ice I_h . It can also be deduced from the I_c structure by a simultaneous rotation of the eight oxygen atoms belonging to the spirals which surround the fourfold cubic axes, and by a shifting of the four remaining oxygens in the plane perpendicular to these axes. Figure 1(g) shows the connection between I_o and ice III. The relationship between the unit-cell basic vectors is $\mathbf{a}_{\text{III}} = 2(\mathbf{a}_2 + \mathbf{a}_3)$, $\mathbf{b}_{\text{III}} = 2(\mathbf{a}_1 + \mathbf{a}_3)$, $\mathbf{c}_{\text{III}} = 2(\mathbf{a}_1 + \mathbf{a}_2)$, and the I_o unit cell contains $\frac{3}{4}$ of disordered oxygen atoms, which order in the sixteenfold tetragonal cell, with eight oxygens filling the tetragonal positions $8b$, the four remaining oxygens occupying the $4a$ positions. In addition to this ordering mechanism, the formation of ice III from I_o requires two combined sets of

displacements which are represented in Fig. 1(g). They consist in a tilting around the fourfold axes of each group of eight oxygen atoms surrounding the middle of the faces of the tetragonal unit cell, and a shifting of the two pairs of remaining oxygens in the antiparallel tetragonal directions $[110]$ and $[\bar{1}10]$. A projection of the shifts in the (001) bcc I_o plane is represented in Fig. 1(h); Fig. 1(i) shows the hydrogen atom distribution in the unit cell of ice III (positions $8b$). The group-theoretical description of the combined ordering and displacive mechanism which transforms I_o in ice III requires two different, four- and six-dimensional, IR's of the O_h^9 group denoted $[\tau_1(\mathbf{k}_{10})$ and $\tau_4(\mathbf{k}_9)$, at the P and N points [$\mathbf{k}_9 = \frac{1}{2}(\mathbf{a}_1^* + \mathbf{a}_2^*)$] of the bcc Brillouin-zone surface.

Ice VI occupies a large area in the phase diagram of ice, as it is stable from about 6 to 20 kbars and from the melt to very low temperatures. The oxygen framework of its tetragonal structure ($D_{4h}^2, Z=10$) was determined by Kamb [14], who stressed the interpenetrating character of its "self-clathrate" type of structure. In our approach the formation mechanism of ice VI and I_o follows an apparently similar scheme to that for ice III. Thus the same IR's of the O_h^9 space group [$\tau_2(\mathbf{k}_{10})$ and $\tau_4(\mathbf{k}_9)$] are involved, but as here the I_o unit cell contains $\frac{5}{8}$ oxygen atoms; the ordering and displacive mechanisms transforming I_o in ice VI occur differently than for ice III, as illustrated in Fig. 2(a). In the sixteenfold tetragonal unit cell of ice VI the oxygens occupy all the vertices of the initially disordered bcc cubes, as well as two among eight cube centers. Besides, the four pairs of oxygen atoms located on the faces of the bcc cubes carry out antiparallel displacements along general low-symmetric directions. Figures 2(b) and 2(c) describe the two types of hydrogen distributions in the ice VI unit cell: Three hydrogens in positions $8g$ and one in position $16h$ are associated with

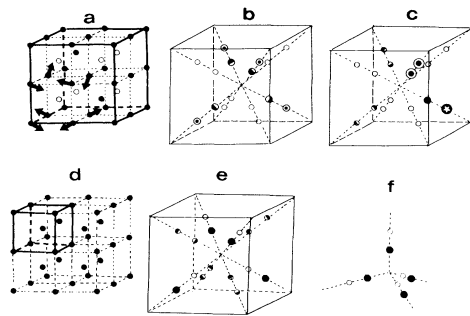


FIG. 2. Ordering and shifting mechanisms transforming I_o into ice VI, ice VII, ice VIII, and ice XI. (a) I_o to ice VI mechanism. (b),(c) Two types of hydrogen distributions around oxygen sites in ice VI. The three types of hydrogen sites with an occupancy $\frac{1}{2}$ are represented by half-filled, centered, and star-shaped circles. (d) Oxygens in the I_o (small cube) and ice VII (large cube) unit cells. (e) and (f) are the hydrogen sites in ice VIII and ice XI, respectively. (f) also represents the hydrogens in ice II.

the oxygens in positions $2a$ and $8g$.

In the structures of ice discussed here, the oxygen frameworks were mainly considered as the distribution of hydrogen atoms was assumed to follow the symmetry created by the transformation mechanisms. By contrast, in ice VII ($O_h^4, Z=2$), which is the high pressure densest form of ice, the structure of which was analyzed by Kamb and Davis [15] in terms of two interpenetrating frameworks of ice I_c , the transformation mechanism from I_o involves exclusively the hydrogen bonds. Figure 2(d) shows that in the I_o unit cell, within the ice VII unit cell, all the positions are filled; i.e., the concentration of water molecules is equal to 1 and I_o is a fully ordered structure. The transformation to ice VII will consist in a reorientation of the hydrogen bonds: The water molecules located at the vertices and at the center of the I_o unit cell become respectively orientationally inequivalent. The hydrogens which are fully disordered in the I_o structure become tetrahedrally ordered, the effective symmetry of water molecules being lowered from O_h to T_d . Figure 1(f) shows the distribution of the hydrogens which occupy the positions $8e$. The $O_h^9 \rightarrow O_h^4$ cell-doubling transition can be described within a standard Landau-type approach: The one-dimensional IR of the O_h^9 space group $\tau_4(\mathbf{k}_{12})$ induces the corresponding breaking of translational symmetry, where $\mathbf{k}_{12} = \frac{1}{2}(\mathbf{a}_1^* + \mathbf{a}_2^* + \mathbf{a}_3^*)$ is the H point of the bcc Brillouin-zone surface. The basic unit-cell vectors are related by the equations: $\mathbf{a}_{VII} = \mathbf{a}_2 + \mathbf{a}_3$, $\mathbf{b}_{VII} = \mathbf{a}_1 + \mathbf{a}_3$, $\mathbf{c}_{VII} = \mathbf{a}_1 + \mathbf{a}_2$.

The formation of three other phases of ice, namely, ice VIII, ice IX, and ice XI, can also be understood on the basis of a positional or orientational ordering of the sole hydrogen atoms, as these phases have similar oxygen frameworks to ice VII, ice III, and ice I_h , respectively. Thus, ice VIII, which is the low temperature form of ice VII, results from a tetrahedral to tetragonal ordering of the hydrogen bonds [16] within the oxygen framework of ice VII. The hydrogens occupy the positions $16h$ as illustrated in Fig. 2(e). The corresponding cell-doubling ferroelastic transition ice VII \rightarrow ice VIII is induced by the two-dimensional IR $\tau_8(\mathbf{k}_{12})$ of the O_h^4 space group, at the R point of the primitive cubic Brillouin zone [11].

Along the same line, orthorhombic ice XI ($C_{2v}^{12}, Z=4$) is the ordered oxygen form of ice I_h , from which it is obtained by cooling below -200°C , provided ice I_h is doped with specific impurities [17]. The ordering of the hydrogen atoms is here a positional one, as shown in Fig. 2(f): In I_h the hydrogens occupy equivalent positions on each part of the hydrogen bonds, while in ice XI only one position ($8b$) is occupied. The ferroelectric-ferroelastic ice $I_h \rightarrow$ ice XI transition is associated with the two-dimensional IR $\tau_{12}(\mathbf{k}_{16})$ of the D_{6h}^4 space group at the center (Γ point) of the hexagonal Brillouin zone [11]. It is still unclear if ice IX, which has the same symmetry as ice III ($D_4^4, Z=12$) [18], constitutes a distinct low-temperature form, more ordered with respect to the hy-

drogen bonds than phase III, as suggested by some authors [18]. To our knowledge, no clear-cut experimental data have proved the existence of an actual isostructural transition between the two phases.

The assumed mechanisms leading to the phases of ice considered herein were analyzed in terms of one symmetry breaking order parameter for purely ordering processes and with two coupled order parameters for combined ordering and displacive mechanisms. Our description of the formation of ice II from I_o is more complex. High pressure ice II ($D_{3d}^5, Z=12$) is obtained on cooling from ice I_h below -50°C and is stable between about 3 and 6 kbars [19]. Although it possesses some resemblance with ice I_h , with similar puckered rings of water molecules, its structure is more compact as was stressed by Kamb [19] and is ordered with respect to the hydrogens. The transformation from I_o to the ice II structure can be described in three stages. The first stage is an ordering of the oxygens which occurs as for the formation of ice I_h : The initial disordered I_o unit cell contains $\frac{2}{3}$ oxygens which order in the $4f$ crystallographic positions, resulting in a bilayered rhombohedral structure with four water molecules per unit cell and a space group D_{3d}^5 . The second stage is a combined mechanism involving a tilting in two opposite directions of the hexagonal rings forming the two layers and an antiparallel shifting of the rings along the [111] rhombohedral direction (the z hexagonal axis) by an amount of $\pm \frac{1}{3} C_{rh}$, where C_{rh} is the lattice vector of the rhombohedral unit cell, along [111]. It produces a decompression of about 10% of the distance between the rhombohedral layers, and a resulting structure which has the same symmetry as ice II ($D_{3d}^5, Z=12$), but with flat in-plane structures. In order to obtain puckered layers, a third mechanism is needed which consists in antiparallel displacements of the oxygens along [111], the magnitude of which is about 10% of $|C_{rh}|$. Figure 2(f) gives the hydrogen positions in the rhombohedral unit cell with two

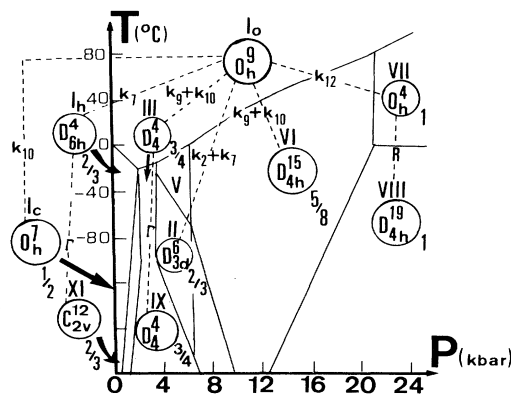


FIG. 3. Relationship between I_o and the various structures of ice for which are indicated the respective concentrations of I_o and the corresponding wave vectors of the bcc Brillouin zone.

hydrogens in $4a$ positions and two others in positions $8b$. The preceding three step mechanisms can be associated with two distinct IR's of the O_h^2 space group [11]: $\tau_1(\mathbf{k}_7)$ for the ordering process and $\tau_1(\mathbf{k}_2)$ for the displacive and tilting mechanisms, where $\mathbf{k}_2 = \frac{1}{9}(2\mathbf{a}_1^* - 2\mathbf{a}_2^* - \mathbf{a}_3^*)$ lies inside the bcc Brillouin zone.

Figure 3 summarizes the connections assumed in this work between the nine structures of ice for which a formation mechanism was proposed, and the I_o parent structure. Three phases of ice, namely, ice IV, ice V, and ice X, do not figure in the diagram of Fig. 3. The structure of ice X which has been reported above 40 GPa [20] is still unknown, and more information is also needed for the metastable rhombohedral ice IV which takes place inside the stability range of ice V. We were unable to find a realistic mechanism for the formation of this latter monoclinic structure ($C_{2h}^2, Z=28$) [21] from I_o .

As shown in Fig. 3, the connection between pressure P and the concentration x of the parent I_o unit cell, and the correlated influence of these two parameters on the structural changes in ice is not straight. Thus, ice I_c , which is the lower pressure structure, coincides with the lowest concentration $x = \frac{1}{2}$. Ice VII corresponds to the highest pressure and maximal concentration $x=1$. Between the preceding extremes the relation between P and x is not monotonous: $x = \frac{2}{3}$ for ice I_h and ice II, $x = \frac{3}{4}$ for ice III, but for the higher pressure structure of ice VI, the concentration decreases to $x = \frac{5}{8}$. This can be explained by the fact that for the formation of ice VI, one needs not only the introduction of additional molecules, but also an exchange of the cubic atoms between filled and vacant positions, which requires additional energy and thus larger pressures.

As a final remark, let us emphasize that our assumption of a parent bcc structure for all the ice structures can be justified by the fact that it is the more compact packing that can be proposed for water molecules when preserving their identity. The formation of close-packed fcc or hcp structures should require the absence of covalent bonds and fully ionic interactions between oxygen and hydrogen atoms, as was noted by Kamb [22]. Thus

unlinked bcc clusters constitute the more easily formed structures in water, when approaching solidification.

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