Reconstruction of ice crystal surfaces at low temperatures

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ABSTRACT

It is generally accepted that the faces of ice crystals in equilibrium with the vapour undergo reconstruction to a quasi-liquid transition film at temperatures above about $-20°C$, though experimental evidence is equivocal. At much lower temperatures it appears that the free energy can be reduced by a less drastic surface reconstruction involving the orientation of surface dipoles to a superlattice. Calculations suggest that this superlattice should be energetically preferred on (0001) basal faces below about 30 K and on (01$\bar{1}$0) prism faces below about 70 K. On (0001) faces, twin boundaries have very low energy and may exist in profusion. The rate of such a reconstruction is probably slow because of the low temperature involved, though molecular interchange with the vapour may facilitate it. It is possible that this structure could be observed by electron diffraction or by fine-focus infrared spectroscopy. A more radical reconstruction is also discussed, but considered to be energetically unlikely.

§ 1. INTRODUCTION

Ordinary ice (ice Ih) crystallizes in a four-coordinated structure which is the hexagonal analogue of the diamond cubic. The oxygen atoms (or ions) lie on the lattice sites, and there is one proton located asymmetrically on each O–H...O bond. Each oxygen has two 'close' protons so that H_2O molecules remain intact. In this structure, initially proposed by Bernal and Fowler (1933), the proton positions are otherwise statistically distributed, leading to a configurational entropy very close to $k \ln (3/2)$ per molecule (Pauling 1935). The unusual properties of this important solid have been extensively studied and documented (Fletcher 1970, Hobbs 1974).

The statistical distribution of protons, or equivalently of water molecule orientations, implies that, for any crystal face, half of the surface molecules will have dipoles with a component directed out of the surface while the other half have their dipole directed inwards. The energy associated with these two orientations is not the same, since the water molecule is not a symmetrical dipole and also has quadratic nonlinearities in its electrical polarizability. It is now generally accepted, as proposed initially by Weyl (1951) and developed in detail by Fletcher (1962, 1963, 1968, 1973), that this leads to a surface phase change as the melting point is approached, the surface relaxing to an orientationally polarized quasi-liquid structure, the thickness of this transition layer increasing as the temperature approaches the bulk melting point. Although a transition layer with a water-like structure and a sharp liquid–solid interface was assumed in the simplified calculations, it is unlikely that either of these assumptions is realistic. The surface transition layer, however, is expected to have a disordered structure, a self-diffusion coefficient intermediate between those of water and ice, and a high electrical conductivity. The most recent paper cited above (Fletcher 1973) still represents the author's current views.

Measurements using proton magnetic resonance (Kvlividze, Kiselev, Kurzaev and Ushakova 1974), photo-emission (Nason and Fletcher 1975), proton channelling (Golecki and Jaccard 1977), mechanical methods (Valeri and Mantovani 1978) and ellipsometry (Beaglehole and Nason 1980, Furukawa 1987) all lend some measure of support to this model, as also does the sharply increasing surface electrical conductivity hear the melting point (Maidique, von Hippel and Westphal 1970). The model suggests that the transition layer exists only above a temperature between about -5 and $-15°C$, depending upon the crystal face exposed, and that the layer thickness is about ten molecular layers at $-1°C$, increasing rapidly as the temperature rises towards $0°C$. Although these experiments generally support the existence of the quasi-liquid layer near the melting point, their indications are not in agreement and none can yet be regarded as definitive. The matter is therefore still somewhat controversial.

It is the purpose of the present paper to examine the likely structure of ice crystal faces in equilibrium with the vapour at temperatures below those for which the quasi-liquid layer is thought to exist. Any such surface reconstruction, as well as being of basic interest, could have significant consequences for the catalytic behaviour of stratospheric ice crystals.

§2. SURFACE RECONSTRUCTION

It is convenient to picture the water molecule as an approximately tetrahedral entity with two of its vertices occupied by protons and two by a density of lone-pair electrons. At temperatures below those associated with surface reconstruction to a quasi-liquid layer for the crystal plane exposed, it is necessary that half of the bonds protruding from the surface are occupied by protons and half by lone pairs. Any deviation from this balance is propagated through the crystal as a macroscopic preferred orientation and raises its free energy prohibitively by reduction of configurational entropy. It is possible, however, to contemplate a surface reconstruction that maintains the orientational balance but reduces the surface free energy through reconstruction to a superlattice. The structures to be proposed below achieve this.

Figure 1 (a) illustrates the oxygen positions in the surface layer of a (0001) basal face. The true surface molecules, shown bold, have one broken bond directed normally from

Fig. 1

(a)   (b)
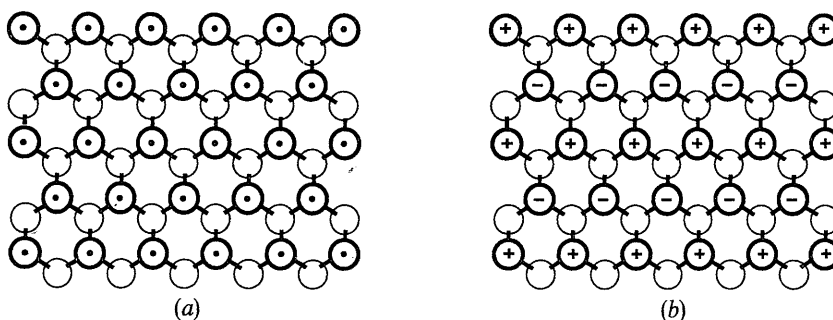
(a) Structure of a normal basal face (0001) of ice. Surface molecules are shown bold. Sticks indicate O–H...O bonds, and black circles on surface molecules indicate broken bonds—either protons or lone-pair electrons. The arrangement of these surface bonds is random, with equal numbers of protonic ($+$) and electron-pair ($-$) bonds. (b) Proposed superlattice arrangement of surface bonds to reduce surface energy. Each bond has four nearest neighbours of opposite sign and only two nearest neighbours of the same sign.

the surface, while the other molecules of the crinkled layer, which lie a little below the surface, are fully bonded into the ice structure. If we neglect the asymmetries of the water molecule that are responsible for driving reconstruction to a quasi-liquid layer near the melting point, then each molecule can be regarded as consisting of four elementary dipoles, each of strength μ, directed tetrahedrally along the two O–H bonds and in the lone-pair directions respectively. The total water molecule dipole μ_w is then

$$\mu_w = 4\mu\cos 52° \approx 3\cdot2\mu, \tag{1}$$

so that, from the experimental value of μ_w,

$$\mu \approx 2 \times 10^{-30}\,\text{Cm.} \tag{2}$$

Dipoles participating in hydrogen bonds to neighbouring molecules can be regarded as balancing out, and we are concerned only with the broken bonds protruding from the surface.

In a random surface, each surface molecule has six neighbouring broken-bond dipoles (on second-neighbours in the crystal structure) and, on average, three of these will be parallel to and three antiparallel to the bond dipole concerned, giving zero electrostatic interaction energy. If the surface is reconstructed to the form shown in fig. 1 (b), however, then each surface dipole has four neighbours of antiparallel orientation and only two of parallel orientation. If the separation between neighbours in the surface is $a \approx 1\cdot6r$, where r is the O–O bond length, then this leads to an electrostatic interaction energy of approximate magnitude

$$\Delta U_B \approx -\frac{\mu^2}{\pi\varepsilon_0 a^3} \approx -2 \times 10^9\,\frac{\mu^2}{r^3}. \tag{3}$$

In calculating this result, the contribution of more distant dipoles has been ignored. The subscript B denotes that the results refers to basal (0001) surfaces.

At the same time, fixing the dipole configurations to the pattern shown in fig. 1 (b) changes the configurational entropy for each surface molecule by an amount

$$\Delta S_B \approx -k\ln 2 \tag{4}$$

while leaving the entropy of molecules in the sub-surface layer essentially unchanged. This surface reconstruction will therefore be favoured, from the point of view of minimizing surface free energy, provided

$$\Delta U_B - T\Delta S_B \approx 2 \times 10^9\,\frac{\mu^2}{r^3} + kT\ln 2 < 0. \tag{5}$$

This condition sets the temperature T_B below which the basal face reconstruction will be favoured. Substituting the numerical estimate (2) for μ and the known bond length $r = 2\cdot76\,\text{Å}$ gives

$$T_B \approx 30\,\text{K.} \tag{6}$$

The configuration shown in fig. 1 (b) is clearly threefold degenerate in orientation. Simple counting of nearest-neighbour orientations shows that both the glide-twin boundary shown in fig. 2 (a) and the mirror-twin boundary of fig. 2 (b) have essentially zero energy penalty, so that they can occur freely in the surface. Other types of domain boundary generally have a significant energy penalty and so are likely to occcur only rarely.

Fig. 2

(a)   (b)
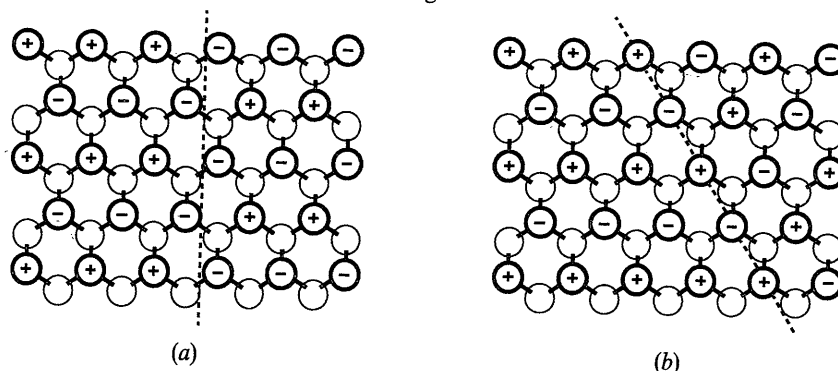
(a) Structure of a glide-twin boundary on a basal face. If a nearest-neighbour orientation count is made across the boundary, then its energy is seen to be approximately zero. (b) Structure of a mirror-twin boundary on a basal face. An orientation count similarly shows the energy to be zero.

Fig. 3

(a)   (b)
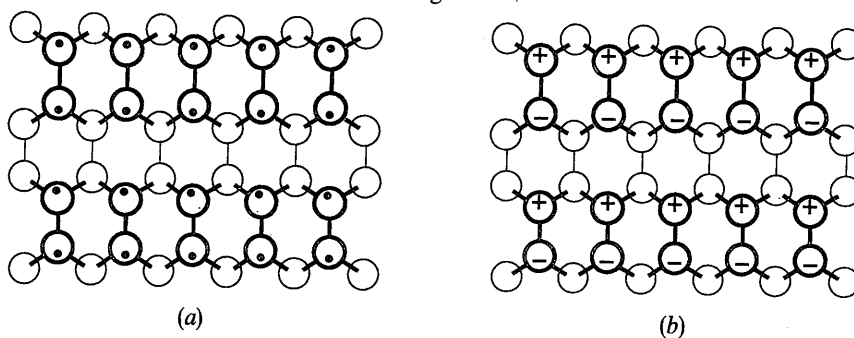
(a) Structure of a normal prism face (01$\bar{1}$0) of ice. Surface molecules are shown bold, and bonds are indicated as before. (b) Proposed superlattice arrangement of surface bonds on this face.

Similar considerations can be applied to exposed (01$\bar{1}$0) prism faces, as shown in fig. 3 (a). Here each row of molecules has a single bond protruding obliquely from the surface, and the proposed low-energy configuration is as shown in fig. 3 (b). Evaluation of the electrostatic interaction energy is a little more complicated in this case, but clearly the result is negative and, to a reasonable approximation,

$$\Delta U_{\mathrm{P}} \approx -\frac{0 \cdot 6\mu^2}{4\pi\varepsilon_0 r^3} \approx -5 \times 10^9 \frac{\mu^2}{r^3}. \tag{7}$$

The entropy reduction is again given by (4), since one bond direction is fixed for each surface molecule, and the prism faces should reconstruct to a superlattice below a temperature

$$T_{\mathrm{P}} \approx 70 \, \mathrm{K}. \tag{8}$$

All domain boundaries on prism faces appear to involve a significant energy penalty, so that they should be much less common than twin boundaries on basal faces.
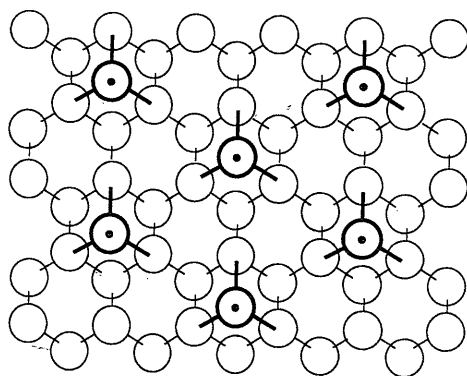
§3. OTHER POSSIBLE RECONSTRUCTIONS

The basal and prism face reconstructions proposed above have been developed simply by examining possible orientational arrangements that are able to minimize electrostatic energy. The near-zero energy penalty associated with twin boundaries on basal faces means that it is possible to consider other superlattice configurations in which these boundaries themselves form an ordered configuration. There are many such possibilities, but none appears to offer any advantage in minimizing free energy. In the case of prism faces, even twin boundaries have an energy penalty, so that no such ordered boundary patterns are favoured.

It is also appropriate to consider the possibility of more radical surface reconstructions in which not just the dipole orientations but rather the whole surface bonding pattern is reconstructed. The existence of many phases of ice with different bonding patterns that are stable at high pressures serves as a starting point for such considerations. As is well known (Fletcher (1970), chap. 3), water molecules remain four-coordinated in all these high-pressure ices, but bond angles suffer significant distortion. Water molecules can be bonded into rings, spirals, or other framework structures, but the limit of bond distortion is that required for bonding to a four-membered ring, as present in ice V which is stable between about 3 and 6 kbar. The only obvious surface reconstruction able to reduce the number or broken bonds is one in which three neighbouring surface molecules on a basal face are bonded to an added molecule located at the centre of their triangle as shown in fig. 4, thus reducing the number of broken bonds by a factor three. Formation of such a structure would involve creation of three four-membered rings for each added surface molecule, with a consequent large balancing energy penalty, although no surface entropy loss is involved. Ordering of the dipoles of the added molecules is unlikely because of their rather large separation.

In view of the high pressure required to stabilize just a small fraction of four-membered rings in ice V, it is clear that the penalty in elastic strain energy involved in such a reconstruction would be very large. It is not possible to decide, without quite detailed molecular calculations, whether or not this reconstruction would be energetically favourable, but this seems rather unlikely.

Fig. 4

A more radical possible reconstruction of basal faces involving adsorption from the vapour of a fractional layer of molecules, shown bold, each bonded to three molecules of the original surface. Such a reconstruction reduces the number of broken bonds in the surface by a factor 3 but involves a great deal of elastic strain.

§4. KINETIC CONSIDERATIONS

It is appropriate to examine the kinetics of transformation from a random to a superlattice surface orientation, to establish whether surface reconstruction of the type we have proposed can be achieved in a reasonable experimental time at the low temperatures necessarily involved.

The mechanism of molecular reorientation in ice involves the formation and motion of Bjerrum defects (Fletcher (1970), chap. 7). These consist of empty (L) and doubly occupied (D) bonds, and are formed in conjugate pairs with an activation energy E_F of about 0·7 eV. The activation energy E_D for diffusion of the defects is about 0·23 eV, the L defects being somewhat more mobile than the D defects, with diffusion coefficient about $5 \times 10^{-10}\,\mathrm{m^2\,s^{-1}}$ at $-10°C$. For pure bulk ice, the orientational relaxation time is about $10^{-4}\,\mathrm{s}$ at $-10°C$ and as long as $10^9\,\mathrm{s}$ at $100\,\mathrm{K}$, so that the question of surface reorientation kinetics does require examination.

A free surface, however, acts as a source and sink of Bjerrum defects, and they can be injected into the crystal singly rather than in pairs. The activation energy E_I for injection would be about $0·5E_F$ except for the fact that the presence of the surface reduces the elastic strain energy associated with each defect, so that E_I is very significantly smaller than this. The activation energy for diffusion is also considerably less than the bulk value for the same reason. It is this injection of orientational defects from the surface that is responsible for the formation kinetics of the quasi-liquid surface layer at temperatures close to the melting point.

At low temperatures the density of intrinsic defects is small, and surface reorientation occurs by injection of a defect at the surface (or, equivalently, by rotation of a surface molecule) followed by its motion along a bond chain until it is annihilated by emergence at another surface molecule. The relaxation time τ for this process is of order

$$\tau^{-1} \approx n^{-2} v_L \exp\left(-E_I/kT\right) \exp\left(-E_D/kT\right), \tag{9}$$

where $v_L \sim 10^{13}\,\mathrm{s^{-1}}$ is the frequency of molecular libration motion and $n \approx 6$ is the number of steps along the bond chain. The calculated relaxation time depends greatly upon the extent to which the activation energies for injection and diffusion of orientational defects are reduced below the related bulk values. In order that the relaxation time at about 70 K be of the order of one minute, so that the reconstructed surface can be easily produced, it is necessary that the activation energies for defect injection and defect diffusion be about 0·3 times the values for bulk ice. Because of the importance of elastic strain in determining these energies, such a reduction seems possible, but no data are at present available. This calculation assumes that the ice is perfectly pure. Any impurities generating Bjerrum defects in the bulk will greatly shorten the relaxation time at low temperatures. The calculation also neglects interaction with the vapour, by which surface molecules are continually removed and replaced by evaporation and deposition, providing a further mechanism for orientational relaxation.

It is not possible to come to a conclusion on this point without further information, but it seems at least a reasonable possibility that surface reconstruction of the type we envision can take place within a practical experimental time and therefore be detectable. The relaxation rate may perhaps be sufficiently slow that kinetic phenomena can be observed but, as with all surface phenomena, such observations can be complicated by adsorption of foreign molecules.

§ 5. Conclusion

This discussion suggests that both the basal faces (0001) and prism faces (01$\bar{1}$0) of ice crystals in equilibrium with the vapour, and by implication other faces as well, undergo orientational reconstruction to an ordered superlattice at sufficiently low temperatures. The reconstruction temperatures are estimated as 30 K for basal faces and 70 K for prism faces. It is difficult to estimate the reconstruction kinetics, but it seems possible that reconstruction may occur in an acceptably short experimental time. It should be possible to detect this reconstruction by electron diffraction or, if the area analysed can be made smaller than the domain size on the surface, by infrared techniques.

While another possible more radical reconstruction is discussed in the text, it seems unlikely that this can lead to a reduction in surface free energy, so that it is not expected to occur.

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