Comment on “Ferroelectricity in Water Ice”†

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Abstract: The weak electrical polarization of thin films of ice vapor-deposited on a metal substrate is unrelated to the proton ordering expected in bulk ice at low temperatures. Criticisms of observations of ferroelectric ordering in KOH-doped ice are unjustified.

At the interface between ice and another material (or a vacuum) a water molecule with a component of its dipole moment directed out of the surface is not energetically equivalent to one oriented the other way, and one therefore expects a small preference for one orientation over the other. As pointed out by Fletcher, the ice rules require that the resulting polarization is propagated into the bulk ice. The penetration of the polarization can only be terminated at appropriately charged protonic point defects, and the depth of penetration is therefore limited by the availability of such defects. There will be a potential difference across the charged double layer so produced, and the properties of such layers in thermal equilibrium have been treated both experimentally and theoretically.

The experiments of Iedema et al., and also those of Su et al., are studying just such properties of thin layers of ice vapor-deposited on a platinum surface. It is misleading to present such experiments in the context of the proton-ordered structure of ice that must, according to the third law of thermodynamics, be the equilibrium state of ice at low temperatures. That structure will be the one of the many possible configurations in the Pauling model which has the lowest energy. Which of the configurations has this property will depend on the interactions of molecules with one another in the bulk of the ice, and the ordering could in principle be either ferroelectric or antiferroelectric in character. The polarizations of less than 1% observed in the experiments of Iedema et al. originate, as they say, from the interface. They are not dependent on the intermolecular interactions in the bulk that favor one proton-ordered structure over another. Moreover, these surface effects can only be ferroelectric in character, oriented one way or the other; there is no equivalent in the thin film experiments to the antiferroelectric ordering that is one of the possibilities in the bulk.

In their paper Iedema et al. discuss a number of experiments by other workers in which proton-ordered ice may have been observed. The ordered phase cannot be produced by cooling pure ice because there is a glass transition at around 100 K, below which ordering is too slow. In alkali hydroxide-doped ices, however, the presence of mobile OH− ions allows bond reorientation to occur, and a first order transition to a new phase called ice XI has been observed at 72 K. Ice Ih has an excess zero point entropy of approximately Rln(3/2) per mole, which was attributed by Pauling to the disorder of the protons. In calorimetric experiments up to two-thirds of this entropy is lost in the transformation, showing that the transition is to a proton-ordered phase, even if the transformation is incomplete. The transformation has also been studied by dielectric measurements and neutron diffraction.

Primarily on the basis of discussion of a thermally stimulated depolarization (TSD) experiment by Jackson and Whitworth, Iedema et al. recommend caution in interpreting any of these experiments as evidence for ferroelectrically proton-ordered ice, but their discussion ignores some of the most relevant facts. First, the TSD experiment must be considered in the context of the other evidence for a phase transition in alkali hydroxide-doped ices at 72 K. This temperature is independent both of the cation and of the amount of doping. In the TSD experiment the depolarization occurs at this temperature and is a consequence of the detransformation. Second, a large depolarization charge is observed only for ice polarized parallel to the c-axis. The sluggish dielectric response which Iedema et al. judge to be the likely explanation of the observations would be isotropic. The sluggish response is probably the explanation of the 100 times smaller depolarization charge that was observed for specimens polarized perpendicular to the c-axis.

However, the real evidence that ice XI is ferroelectrically ordered comes from the neutron diffraction experiments, which are dismissed by Iedema et al. without serious discussion. High-resolution lattice parameter measurements show that there are two phases in the transformed ice: the untransformed ice Ih and the ice XI. Single-crystal measurements show that the ice XI component has a C-centered 8-molecule unit cell, and for the ice structure this immediately implies that all bonds parallel to the c-axis are ordered in the same direction. This feature is independent of any problems concerning the closer refinement of the structure, and it proves unambiguously that the structure is ferroelectrically ordered. Antiferroelectric ordering would produce additional diffraction peaks which are definitely not present. In retrospect the TSD experiment can be seen as a macroscopic confirmation of the ferroelectric character of ice XI.

Iedema et al. state that for ferroelectric ordering the permittivity should vary as \( C(T - T_0) \), and they attempt to infer something about this from the TSD data. However, this form of temperature dependence with positive \( T_0 \) has already been reported for fields along the c-axis both in KOH-doped ice and in pure ice. For fields perpendicular to the c-axis \( T_0 \) is insignificantly different from zero. According to the theory of the transition developed by Minagawa, a positive \( T_0 \) is indicative of ferroelectric interactions between the molecules and its value is expected to be less than the transition temperature, so that there is no divergence of the permittivity at the transition.

The following conclusions are fully compatible with the whole of the experimental evidence:

1. The phase formed by annealing alkali hydroxide-doped ice below 72 K is the proton-ordered form of ice Ih, and it was justifiably named “ice XI”. It is a bulk property of the ice, and the dopant acts as a catalyst in a perfectly understandable way.

Early indications of ferroelectric effects at higher temperatures are related to sluggish polarization and the glass transition; there are no other “under-identified ferroelectric ices”.

2. The ordering in ice XI is ferroelectric in character along the \( c \)-axis, in agreement with the sign of \( T_0 \) in the temperature dependence of the paraelectric permittivity. It is worthy of note that this evidence for ferroelectric-type interactions is observed in pure as well as doped ice.

3. The small polarizations observed in vapor-deposited layers of ice are an expected property of the surface and provide no evidence about proton ordering in bulk ice at low temperatures.

References and Notes