Dielectric Behavior of Cubic and Hexagonal Ices at Low Temperatures*

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Cubic ice Ic and hexagonal ice Ih were prepared in pressurizable dielectric cells at temperatures near −110°C from the high-pressure ices II and IX. No differences were found between the dielectric properties of Ic and Ih. Freshly prepared samples exhibited longer relaxation times at low temperatures than those commonly found for samples of Ih prepared directly by freezing purified water. These long relaxation times became appreciably shorter with sample aging. These results are attributed to precipitation of impurities from ices II and IX, followed by their gradual reincorporation in the ice I lattice. At temperatures as high as −50°C the isothermal sequence of transformations I→II→I is capable of producing a substantial degree of purification of ice I in terms of its dielectric relaxation time.

The dielectric properties of most of the known phases of ice have been characterized,[1–4] at least in part. Ices II and IX show no dielectric dispersion attributable to molecular reorientation[2,4] and are orientationally ordered. Among the disordered phases which exhibit such dispersion ordinary hexagonal ice Ih is the slowest to relax. Dielectric measurements of cubic ice Ic have not been reported previously.

Ic is structurally similar[5] to Ih, with an almost identical arrangement of nearest neighbors and, by reason of symmetry, is also fully disordered with respect to the statistical distribution of each molecule over the six orientations consistent with full hydrogen bonding.[6] The cubic structure is sometimes chosen for simplicity to represent hexagonal ice in models of relaxation.[7,8] Such a substitution is bound to yield the single dielectric relaxation time required by application of the Bjerrum mechanism of relaxation to a structure of the symmetry of Ic. Symmetry alone puts no such requirements on Ih, although measurements of the "best" samples have shown no detectable departure from a single relaxation time, at least at relatively high temperatures.

The present dielectric study of cubic and hexagonal ices was undertaken in an attempt to compare their relaxation rates and static permittivities.

The classical method[9] of preparing Ic by condensation of water vapor *in vacuo* on a surface cooled below −100°C is not a convenient source of the quantities of ice required for dielectric study. Instead, we made use of the discovery of Bertie, Calvert, and Whalley,[10] that cubic ice may be formed from various high-pressure polymorphs of ice, to simply prepare samples within the dielectric cell.

The irreversible transformation[11,12] of Ic to Ih ice at temperatures above about −90°C limited the measurements to temperatures where the relaxation is relatively slow. However, the presence of the transformation itself made possible direct comparison of the properties of cubic and hexagonal ice derived from the same sample. This is important since the properties of hexagonal ice itself have not been defined at these low temperatures, and even at temperatures

as high as −40°C there is a considerable variability in the results reported by different authors and for different samples.[1,13–15] Evidence is presented below that fresh samples of Ih prepared from ices II and IX are generally dielectrically purer, in the sense that they show slower relaxation rates, than samples prepared by careful freezing of highly purified water.

## EXPERIMENTAL METHODS

Dielectric Cells

Cubic ice and most samples of hexagonal ice were prepared and measured in one of two cells (Fig. 1), described in detail below, designed for insertion in the same steel pressure vessel B on which was shrunk a $\frac{1}{4}$-in. thick cylindrical ring C of Teflon for external thermal lagging.

In the coaxial cell [Fig. 1(a)] the central electrode D of 304 stainless steel was supported on the hardened AISI 4340 steel guard electrode F by epoxy resin E which also served as a pressure seal and insulation for the low-potential lead G. I was mica insulation. The hardened steel piston A contained a thermocouple L and was insulated from the press by a sheet of Bakelite. Liquid-tight seals were achieved by the rubber O-ring K and plug M, both supported by triangular backing rings J of 2%-Be copper. The cell constant was approximately 1.2 pF.

During some runs evidence was found of a considerable pressure gradient along the axis of this cell. A sample of ice II at 3 kbar prepared by squeezing Ih below −50°C showed a small persistent dispersion region, which was attributed to the presence of unconverted Ih in the electrode region. Thereafter nearly all pressure applications were made at temperatures above −30°C. Frictional effects were reduced by replacing the $\frac{1}{10}$-in. thick rubber plug M by a $\frac{1}{2}$-in. plug of Teflon. During the II→I transformation (a volume increase of 25%) D was sometimes dislodged and lead G broken.

In the parallel-plate cell [Fig. 1(b)] the two opposed tool-steel pistons A each carried a circular electrode D of 304 stainless steel. E was mica insulation. En-

FIG. 1. High-pressure dielectric cells: (a) coaxial cell; (b) parallel-plate cell.

I inch

(a)   (b)
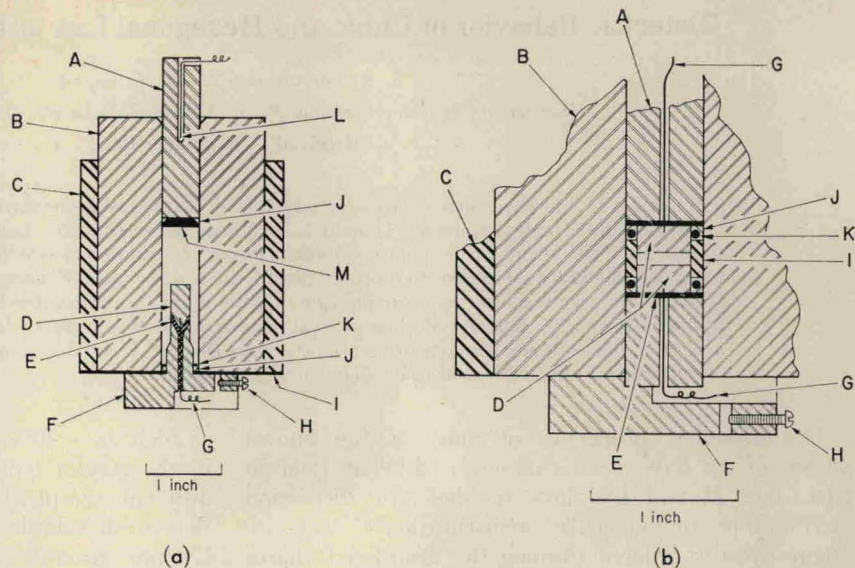
ameled copper leads G to the electrodes through the pistons were further insulated with Teflon spaghetti and soldered to coaxial cables whose shields were firmly anchored by the screws H. The sample was contained by the Teflon ring I which also served to keep the electrodes apart during assembly. The thermocouple was inserted between B and C. Cell constants were of course variable and were obtained for the phase present from capacitances measured at appropriately high frequencies and known[1,2,4] values of the high-frequency permittivity ϵ_∞.

Control of Pressure and Temperature

Pressures up to 3 kbar were generated by a compressed-air-driven oil pump and were read on calibrated Heise gauges. They were transmitted to the cell by a capped hollow steel ram driven by a simple piston–cylinder arrangement adapted from a design of Whalley.[4] Temperature was regulated by thermistor-controlled flow of liquid nitrogen through a copper coil placed in the isopentane bath (f.p., $-160°C$) into which the pressure vessel and lower end of the press were immersed. Temperature variation during the thermostat cycle was not more than 0.1°C at the site of the thermocouple.

Electrical Measurements

Capacitance and conductance were measured in the frequency range between 0.02 Hz and 500 kHz, as described previously.[16,17]

Preparation of Samples

Freshly degassed conductivity water was initially pressurized to about 100 bars before immersion of the cell in the cooling bath to prevent the possibility of contamination by the bath liquid. The pressure

was then raised to about $2\frac{3}{4}$ kbar and ice III formed by cooling to about $-28°C$, where it was conditioned for at least 20 h. Ice II was formed by cooling III to $-60°C$ and then conditioning at $-35°C$.

Ice I[18] was prepared by cooling either III (rapidly to prevent conversion to II) or II to about $-155°C$, reducing the pressure to about 100 bars,[19] and raising the temperature. Depressurized III (more strictly IX)[4] transforms to Ic between -120 and $-105°C$, and II between -110 and $-95°C$, the details depending on the heating rate and sample history.[10] Figure 2 shows the change of ϵ_∞ during typical transformations, and the lower part of Fig. 3 shows the gradual growth of the dispersion of ice I made from ice II.[20] Commonly the transformation was followed by monitoring both the change in volume and the change in high-frequency capacitance.

Identification of Cubic Ice

In view of the slow transformation of cubic to hexagonal ice at temperatures not much above the temperatures at which cubic ice forms from the high-pressure polymorphs, we were in a few cases not sure which ice I was present. In general, however, reasonable inferences about the phase present could be made from the criteria of Dowell and Rinfret[11] and Calvert[21] which relate the Ic to Ih transformation rate to temperature and sample history. In three cases these inferences were confirmed by x-ray powder analysis of samples extracted from the parallel-plate cell at low temperatures after dielectric measurements had been made. These samples were Ic, Ic containing about 10% Ih, and Ih. (Small amounts of Ic in Ih would not have been detected.) A fourth sample showed the presence of some II in Ih as expected from its dielectric behavior, indicating some lack of hydrostaticity in this cell at low temperatures.