Dielectric Behavior of Cubic and Hexagonal Ices at Low Temperatures*

S. R. GOUGH AND D. W. DAVIDSON

Division of Chemistry, National Research Council of Canada, Ottawa, Canada

(Received 14 November 1969)

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.

(a)   (b)
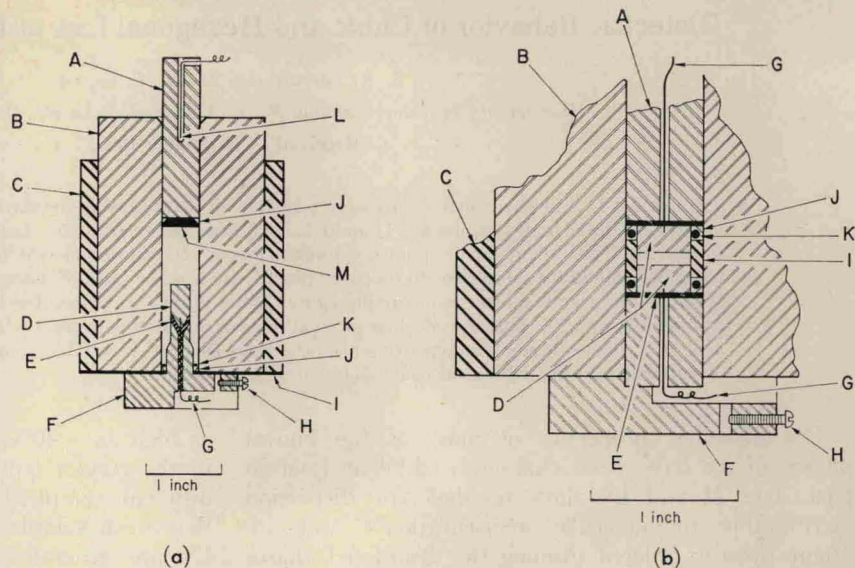
ameled copper leads G to the electrodes through the pistons were further insulated with Teflon spaghetti and soldered to coaxial cables whose shields were firmly anchored by the screws H. The sample was contained by the Teflon ring I which also served to keep the electrodes apart during assembly. The 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.
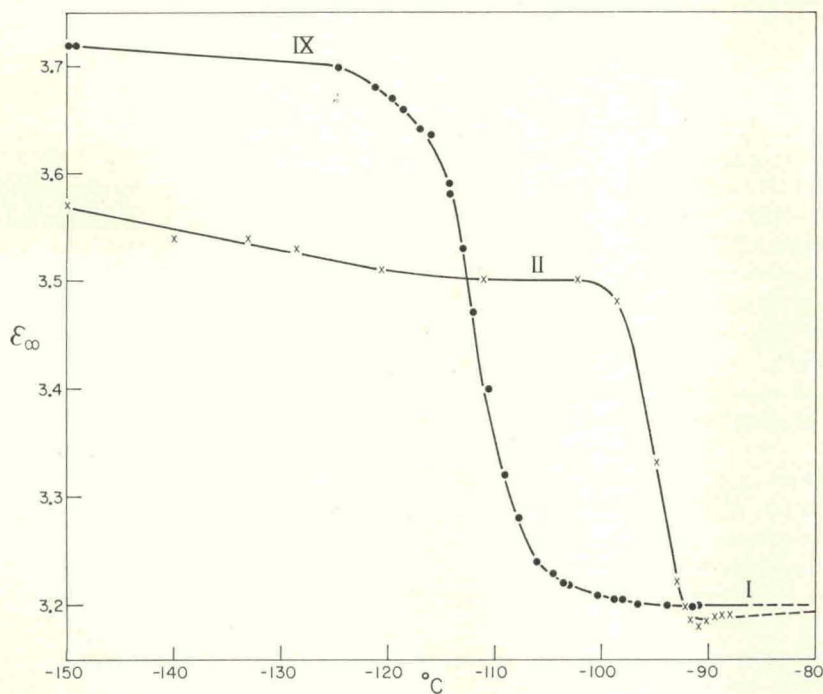
FIG. 2. Changes in permittivity at 50 kHz accompanying heating and transformation of ices II and IX to ice I at 110 bar in the parallel-plate cell. Heating rate was about 0.5 deg/min. Changes of cell constant resulting from thermal expansivity have been ignored.
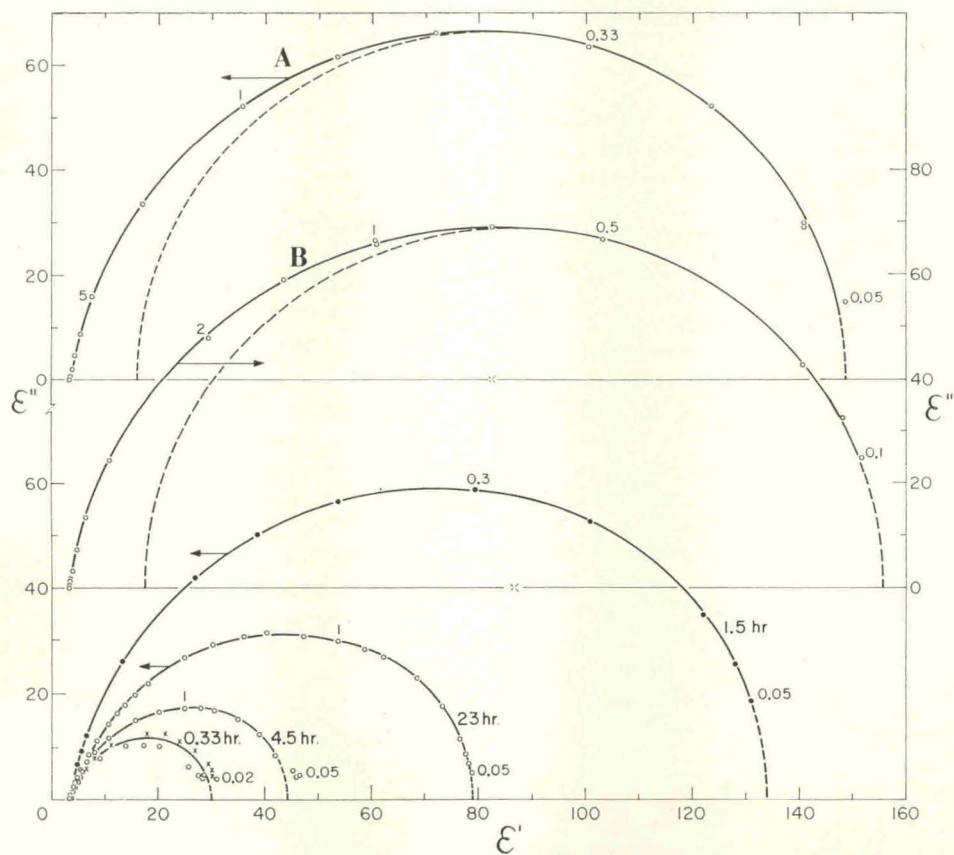

FIG. 3. Cole–Cole plots: A, cubic ice at −88.0°C and 110 bar; B, hexagonal ice at −86.5°C and 1 bar. The lower loci show the dispersion at various times from the start of the II→Ic transformation in the coaxial cell at −86°C. Numbers beside points are frequencies in hertz. See Ref. 20.

RESULTS

Twelve different samples were studied and 45 complex permittivity loci obtained. In none of the measurements were any changes in dielectric properties found which could be related to the change from cubic to hexagonal ice. This conclusion is based on examination of the time and temperature dependence of the static permittivity and relaxation properties of individual samples, rather than intercomparison of samples whose relaxation behavior showed considerable variation (see below) and where the biggest contributing error to the static permittivity was uncertainty in cell constant. A change of static capacitance of 2% or 3% and of relaxation time of 10% would probably have been detected.

Although Maxwell–Wagner polarization characteristic of the coexistence of two phases of different dielectric properties was clearly seen at low frequencies during the II to Ic and III to Ic transformations, no such effect could be identified with the Ic to Ih transformation.

The results which have been chosen for presentation below refer in large part to polycrystalline hexagonal ice. The evidence is, however, that samples of cubic ice which are similar in homogeneity and purity exhibit substantially the same dielectric behavior.

Complex Permittivity Loci

The nature of the Cole–Cole plots is illustrated in Fig. 3. Locus A refers to a freshly prepared sample, undoubtedly of Ic, measured in the parallel-plate cell and locus B to a sample of Ih in the coaxial cell. These shapes are representative of those invariably obtained for samples prepared from high-pressure polymorphs, which never showed exact Debye behavior. The low-frequency side could usually be fitted accurately by a semicircle but ϵ'' approached the permittivity axis at high frequencies at an angle somewhat less than 90°. These shapes could be approximated by either the superposition of two Debye relaxation processes, or somewhat better, by the skewed arc representation.[22] The degree of skewness varied from sample to sample; the largest value of β observed was about 0.90. There was generally no appreciable overlap at low frequencies from space–charge effects.

The series of loci in the right half of Fig. 4 show the change of shape with increasing temperature for a sample prepared from ice II and conditioned for 36 h near −90°C to ensure complete conversion to Ih. Increase in temperature was accompanied by some irreversible increase in skewness.

The same kind of skewness may also occur in the loci of samples of Ih prepared directly by freezing water. The sample illustrated in the left half of Fig. 4, measured in a conventional cell at atmospheric pressure, showed Debye loci above about −35°C, but skewness developed at lower temperatures. The

behavior was reversible upon increase of temperature again.

Static Permittivities ϵ_0

The static permittivities were obtained from Debye semicircles (cf. Figs. 3 and 4) drawn to fit the low-frequency side of the experimental loci. The results are shown in Fig. 5. Data obtained with the conventional cell did not extend below 20 Hz and these values (O) of ϵ_0 are subject to extrapolation error below −50°C, as are all values near −90°C and lower. Our values are generally appreciably higher than those of Auty and Cole[1] but agree quite well with the more recent data of Cole and Wörz.[14] The "best" straight line given by a plot of $(\epsilon_0-\epsilon_\infty)^{-1}$ vs T for our polycrystalline data (equivalent to the curve drawn in Fig. 5) yields $A=22050$ and $T_\infty=32°K$ in the equation $\epsilon_0-\epsilon_\infty=A/(T-T_\infty)$. The Cole and Wörz values were $A=20715$ and $T_\infty=38°K$ for their zone-refined single-crystal sample 13C above −65°C. In the experiments of Cole and Wörz the applied field was normal to the c axis. Our 3% larger values of ϵ_0 over the range of temperature common to the two studies formally yield an anisotropy in ϵ_0 of about 9%, but we hesitate to assume that the combined experimental error is significantly smaller than 3%.

Since our samples of ice I were usually prepared at low temperatures and measurements made with temperature increasing, the experimental values of ϵ_0 generally showed no evidence of formation of the cracks or gaps which are difficult to avoid when ice samples are subjected to thermal contraction. The applied pressure of 110 bar did not always prevent the development of gaps when our samples were cooled. A gap evident from the low value of ϵ_0 of one sample at −51°C and 110 bar was closed by temporarily raising the pressure to 800 bar.

Relaxation Times

Relaxation times, taken as the reciprocals of the angular frequencies of maximum absorption, are shown in Fig. 6, along with some of the data of Auty and Cole.[1] The open circles refer to the same sample of Ih as Fig. 4 (left), open symbols below −85°C refer mostly to Ic, the remainder to Ih. Measurements were generally made with temperature increasing.

Relaxation times of samples prepared from high-pressure forms invariably decreased irreversibly with the passage of time. This is illustrated in Fig. 6 by the solid circles at temperatures corresponding to the vertical dashed lines. Measurements at the same temperature were separated by intervals of 12–18 h. During these periods there were only small drifts at −92.5 and −86.5°C, a much greater drift at −58.3°C, and finally little change at −42.5°C. When the temperature was lowered to −85.2°C (actually between the two measurements at −42.5°C) the relaxation
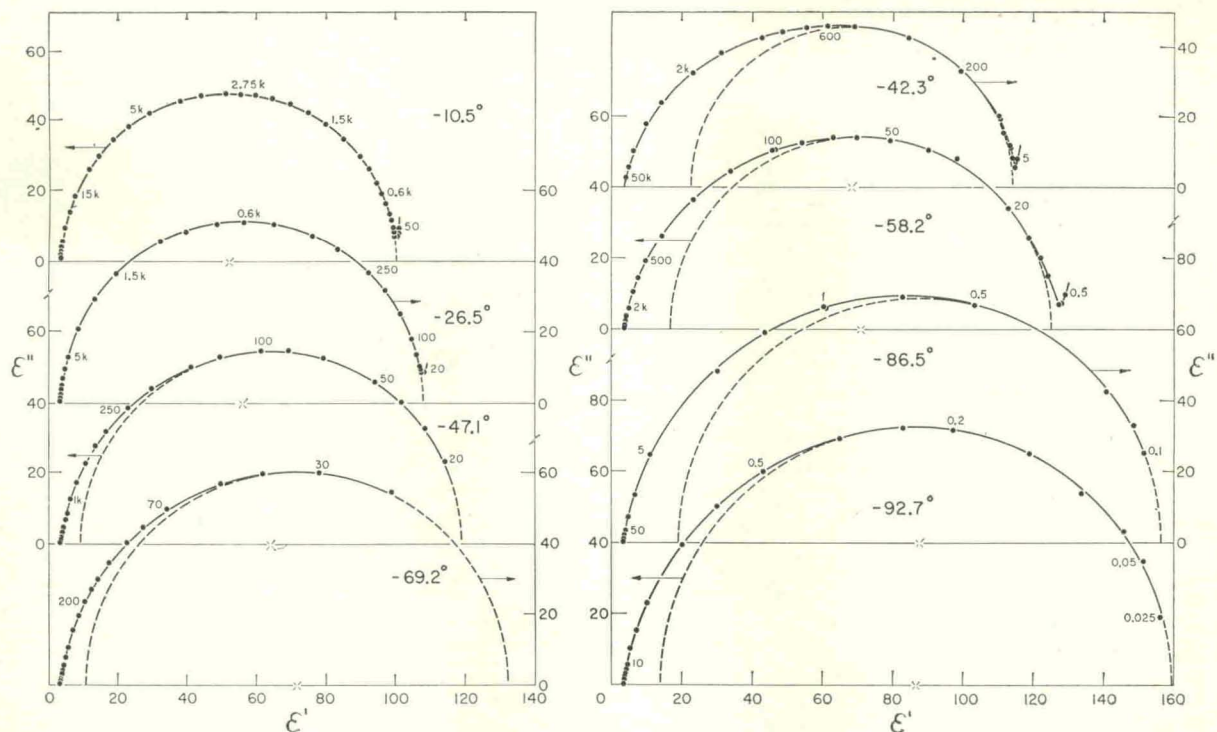
FIG. 4. Cole–Cole plots for hexagonal ice prepared (left) by freezing liquid water and (right) below −100°C by depressurizing ice II. Semicircles are drawn to suggest the extent of departure from single relaxation time behavior.

time was some 40 times smaller than the initial value at −86.5°C.

This drift tended to interfere with attempts to measure the pressure coefficient of the relaxation time. Values of the activation volume were nevertheless estimated to be 1.8 ± 0.6 cm³/mole at −87°C and, for a sample relaxing some 15 times as fast as the Auty–Cole rate, 0.6 ± 0.5 cm³/mole at −40°C.

Effect of the I→II→I Cycle on the Relaxation Times

Several experiments were made to determine the effect on relatively rapidly relaxing samples of conversion to II and back to I at a number of fixed temperatures, including some so high that Ic was probably never present. Samples of Ih in the parallel-plate cell were first annealed at −30°C and 110 bar

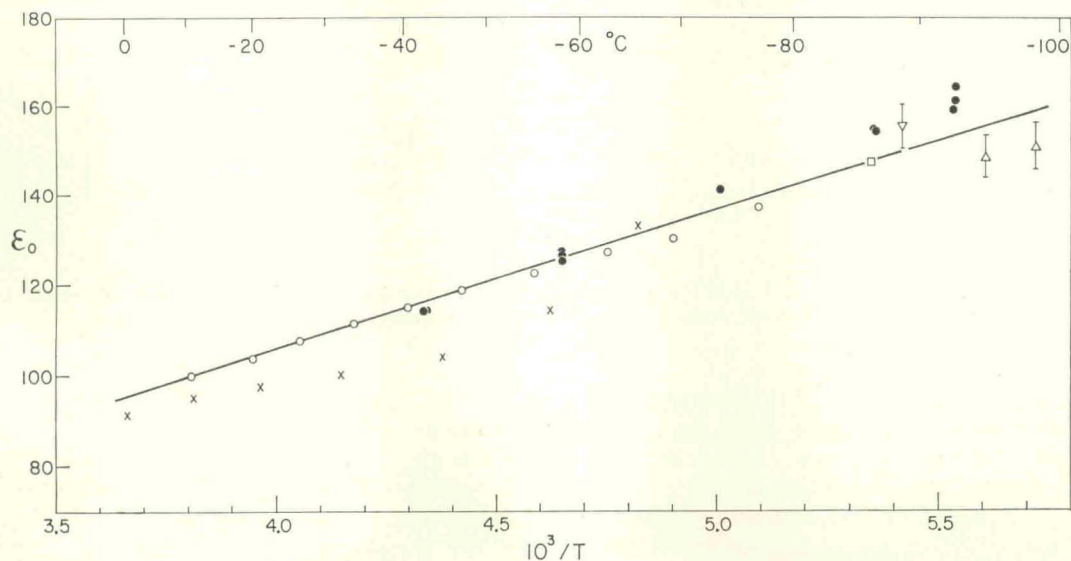FIG. 5. Static permittivities of hexagonal ice: ×, data of Auty and Cole[1]; O, sample frozen from liquid; otherwise samples prepared from ice II or IX in the coaxial cell.
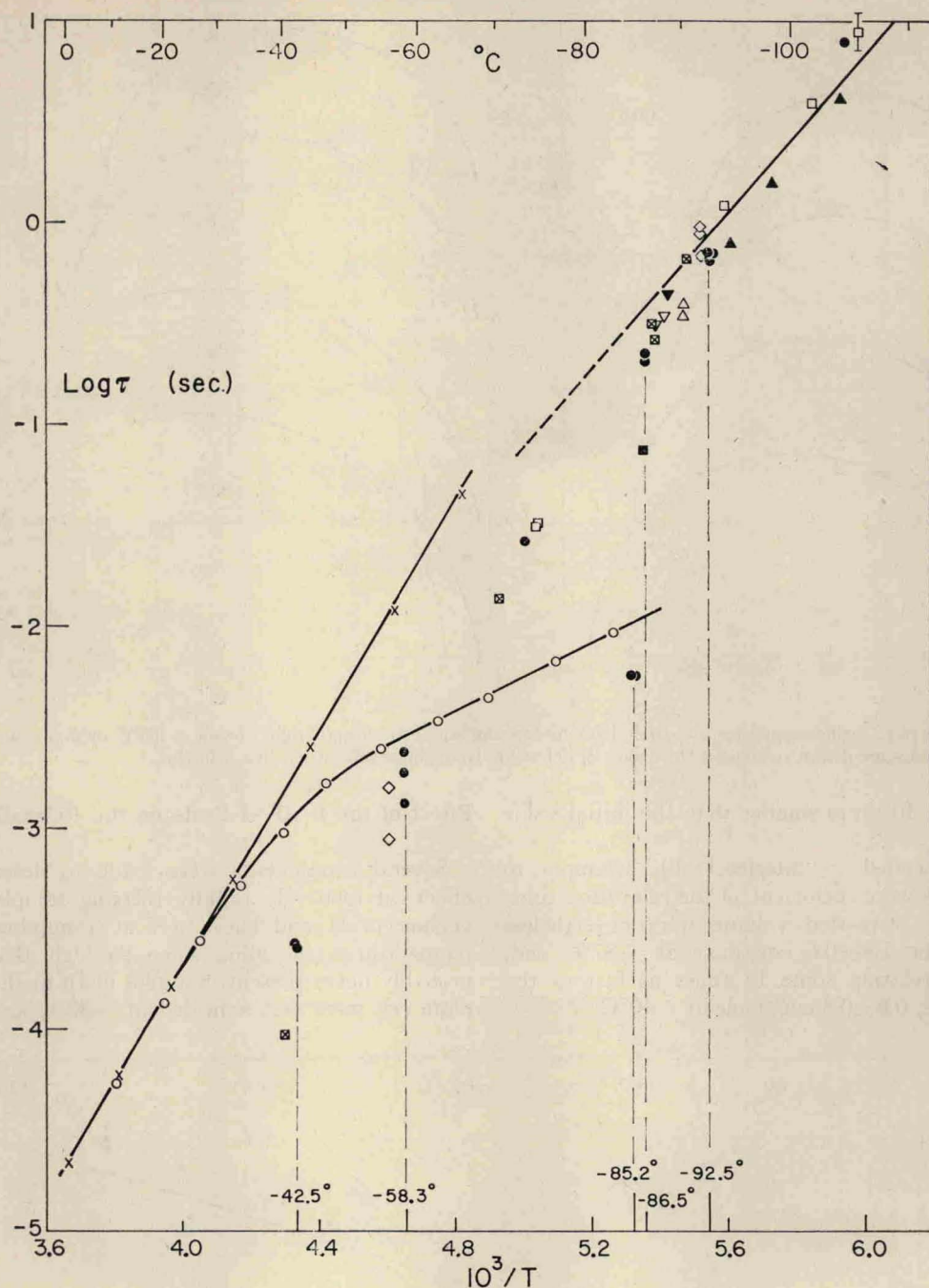
FIG. 6. Dielectric relaxation times: $\times$ and $\bigcirc$ as in Fig. 5, remaining points for samples prepared from high-pressure forms in coaxial cell (solid symbols) or parallel-plate cell (open symbols).

for 24 h. The temperature was then lowered to the desired value where it was held fixed during the following sequence of operations. Initial dielectric measurements were made at 110 bar, the pressure was raised to $2\frac{3}{4}$ kbar for at least 12 h to ensure complete conversion to II, the sample was reconverted to I, and new measurements were made at 110 bar after an equilibration period of 20 min and again after

12 h. The relaxation times measured at three temperatures are given in Table I.

The newly transformed samples at -51 and $-70°C$ were unboubtedly Ih. At $-92°C$ the lifetime of Ic is ≈ 100 min,[11,21] and the sample measured shortly after the transformation was likely Ic or a mixture of Ic and Ih.

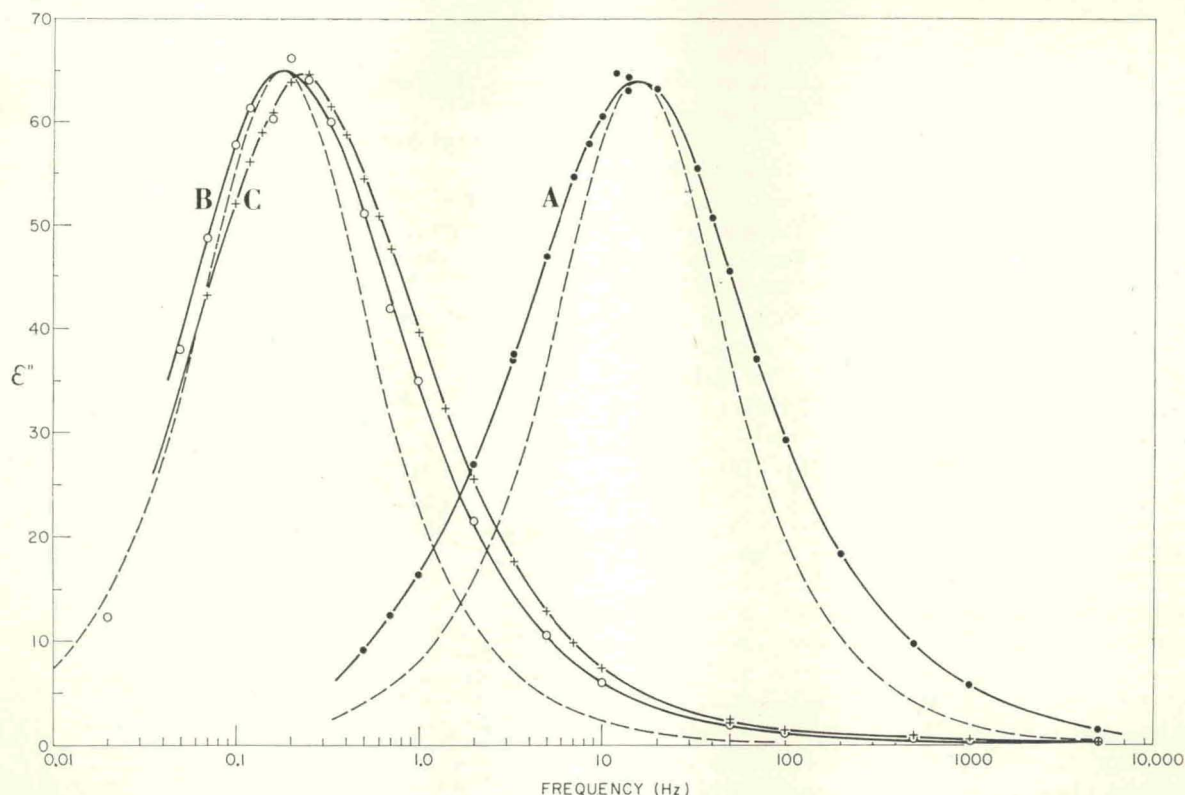It is apparent that the transformation sequence

FIG. 7. Effect of I→II→I cycle at −92°C on a sample in the parallel-plate cell. A, original sample; B, newly transformed sample; C, sample B aged 12 h. Dashed lines show Debye absorption curves.

resulted in a marked increase in relaxation time, followed by the same temperature-dependent drift of τ toward shorter times observed in samples of Ih prepared via Ic from II or IX at temperatures near −110°C.

As illustrated in Fig. 7, the absorption by samples reconverted at low temperatures was more nearly Debye-like than before the transformations. The opposite was true of samples reconverted to ice I at higher temperatures.

DISCUSSION

A fall in the temperature dependence of the relaxation time like that shown by points ○ in Fig. 6 appears to have been observed at low temperatures in all previous studies of hexagonal ice which extended to low enough temperatures. At higher temperatures there is general agreement[13–15,23] with the data of Auty and Cole.[1] However, the temperature of departure from the high-temperature linear behavior varies with the sample, occurring for example at about −30°C in our case, at about −40°C in the case of Cole and Wörz,[14] and at various temperatures between −40 and −60°C for different samples of Ruepp and Käss.[15] The common explanation of this behavior is that at low temperatures extrinsic Bjerrum defects, probably generated by impurities, outnumber the intrinsic defects associated with the ideal lattice. If this is so, a dielectric criterion

of the quality or dielectric purity of the sample may be based on the smallness of the departure at low temperatures from the expected intrinsic relaxation times: The larger the relaxation time, the better the sample.

Our low-temperature relaxation times may be compared with data in two recently published studies. The relaxation times obtained by von Hippel et al.[13] for various samples of zone-refined ice at temperatures between −70 and −90°C are scattered about (mostly below) the dashed extrapolation of our low-temperature line (Fig. 6). One sample gave a relaxation time at −78°C close to the extrapolated Auty–Cole line but a dispersion amplitude ($\Delta\epsilon = 243$) in no way consistent with our and other static permittivity data. The large τ and $\Delta\epsilon$ values seem to be an artifact of the

TABLE I. Effect of the I→II→I transformation cycle on relaxation times.

Temp (°C)	$\tau \times 10^5$ (sec)		
	Original sample	Newly trans-formed sample	Transformed sample after 12 h
−51	38	160	88
−70	39	250	⋯
−92	990	88 000	69 000

analysis. A single result (for the same sample) at a much lower temperature ($-133°C$) gave a more reasonable $\Delta\epsilon = 167$ but a relaxation time smaller by a factor of 60 than the extrapolation of our line to lower temperatures.

For highly purified ice, Ruepp and Käss[15] show two relaxation times near $-70°C$ which are larger by a factor of 2 than given by the dashed line of Fig. 6.

We conclude from these and other comparisons that ice I freshly prepared from ice II or IX frozen from relatively impure water is of comparable purity, in the dielectric sense, to the purest samples of ice which have been obtained directly from elaborately purified and carefully frozen water. Direct evidence that considerable purification is achieved by transformation to ice II and back again is provided by Table I.

It seems likely that impurities to which the dielectric properties are sensitive are much less soluble in ice III (or IX) and II than in ice I and separate from these phases during their formation and conditioning, perhaps to collect at interfaces between microcrystals. The precipitation of ionic impurities from freshly prepared ices VI and VII has been previously reported.[3] The time dependence of the low-temperature relaxation times may then be attributed to reincorporation of impurities into the bulk of the sample. Departures from simple Debye semicircular loci are to be expected from a nonuniform distribution of impurity centers, and therefore of extrinsic Bjerrum defects, through the sample. The observed skewness on the high-frequency side of the loci accords with the faster relaxation near impurity centers.

Under conditions where most of the Bjerrum defects are generated by impurities it is not surprising to find that the apparent volumes of activation for relaxation (like the energies of activation) are appreciably less than the values—2.9[24] and 3.8[25] $cm^3 mole^{-1}$ at $-25°C$— found at higher temperatures where the relaxation is intrinsic.

Gränicher has recently suggested[26] that there is a real change in relaxation mechanism at temperatures between -40 and $-60°C$ from one determined by Bjerrum orientational defects at higher temperatures to one in which intrinsic ionic defects play the dominant role. In this view, the change in temperature dependence of the relaxation time in this temperature range persists in ice of negligible impurity.

Insofar as our low-temperature results show by the shapes of the dispersion–absorption loci that impurities are still affecting the relaxation behavior of the best samples, it is likely that the proper intrinsic relaxation in the vicinity of $-100°C$ is considerably slower than has yet been observed. We incline to the view that with increased purity the region of change of slope, already near $-70°C$, will shift to still lower temperatures. It is possible that a combination of the usual purification

techniques with freezing to a high-pressure ice will provide the purity required to test these views.

As to the nature of the impurities, we can only surmise that in the present samples they consisted mainly of the components of air. Molecules of nitrogen and oxygen are not greatly larger than water molecules and are known to slowly diffuse through hexagonal ice. There is evidence[17] of their ability to substitute for water molecules in clathrate hydrates. It is also possible that extrinsic Bjerrum defects originate in significant numbers at the interfaces in highly polycrystalline samples.

ACKNOWLEDGMENTS

* Issued as NRCC No. 11211.
[1] R. P. Auty and R. H. Cole, J. Chem. Phys. **20**, 1309 (1952).
[2] G. J. Wilson, R. K. Chan, D. W. Davidson, and E. Whalley, J. Chem. Phys. **43**, 2384 (1965).
[3] E. Whalley, D. W. Davidson, and J. B. R. Heath, J. Chem. Phys. **45**, 3976 (1966).
[4] E. Whalley, J. B. R. Heath, and D. W. Davidson, J. Chem. Phys. **48**, 2362 (1968).
[5] K. Lonsdale, Proc. Roy. Soc. (London) **A247**, 424 (1958).
[6] G. Honjo and K. Shimaoka, Acta Cryst. **10**, 710 (1957).
[7] L. Onsager and M. Dupuis, in *Electrolytes* (Pergamon Press, Inc., London, 1962), p. 27.
[8] L. Onsager and L. K. Runnels, J. Chem. Phys. **50**, 1089 (1969).
[9] See references quoted in Ref. 5.
[10] J. E. Bertie, L. D. Calvert, and E. Whalley, J. Chem. Phys. **38**, 840 (1963); Can. J. Chem. **42**, 1373 (1964).
[11] L. G. Dowell and A. P. Rinfret, Nature **188**, 1144 (1960).
[12] R. H. Beaumont, H. Chihara, and J. A. Morrison, J. Chem. Phys. **34**, 1456 (1961).
[13] A. von Hippel *et al.*, "The Dielectric Relaxation Spectra of Water, Ice and Aqueous Solutions," M.I.T. Tech. Rept. 6, 1969.
[14] (a) R. H. Cole and O. Wörz, in *Physics of Ice* (Plenum Press, Inc., New York, 1969), p. 546. (b) O. Wörz and R. H. Cole, J. Chem. Phys. **51**, 1546 (1969).
[15] R. Ruepp and M. Käss, Ref. 14(a), p. 555.
[16] A. D. Potts and D. W. Davidson, J. Phys. Chem. **69**, 996 (1965).
[17] S. R. Gough, E. Whalley, and D. W. Davidson, Can. J. Chem. **46**, 1673 (1968).
[18] We use ice I here and elsewhere when there is no reason to distinguish between Ih and Ic.
[19] A pressure of this magnitude was normally maintained to act against the development of gaps in the sample.
[20] The three loci at lower left show a very slow transformation rate because of slow relaxation of the pressure built up in the coaxial cell by the transformation itself. The faster transformation at right occurred when the clamps holding the cell were released. Points × refer to increasing, ○ to decreasing frequency, ● to the mean of both.
[21] L. D. Calvert (private communication).
[22] D. W. Davidson and R. H. Cole, J. Chem. Phys. **19**, 1484 (1951).
[23] F. Humbel, F. Jona, and P. Scherrer, Helv. Phys. Acta **26**, 17 (1953).
[24] R. K. Chan, D. W. Davidson, and E. Whalley, J. Chem. Phys. **43**, 2376 (1965).
[25] H. Gränicher, Ref. 14(a), p. 534.
[26] Reference 14(a), p. 1.