

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.

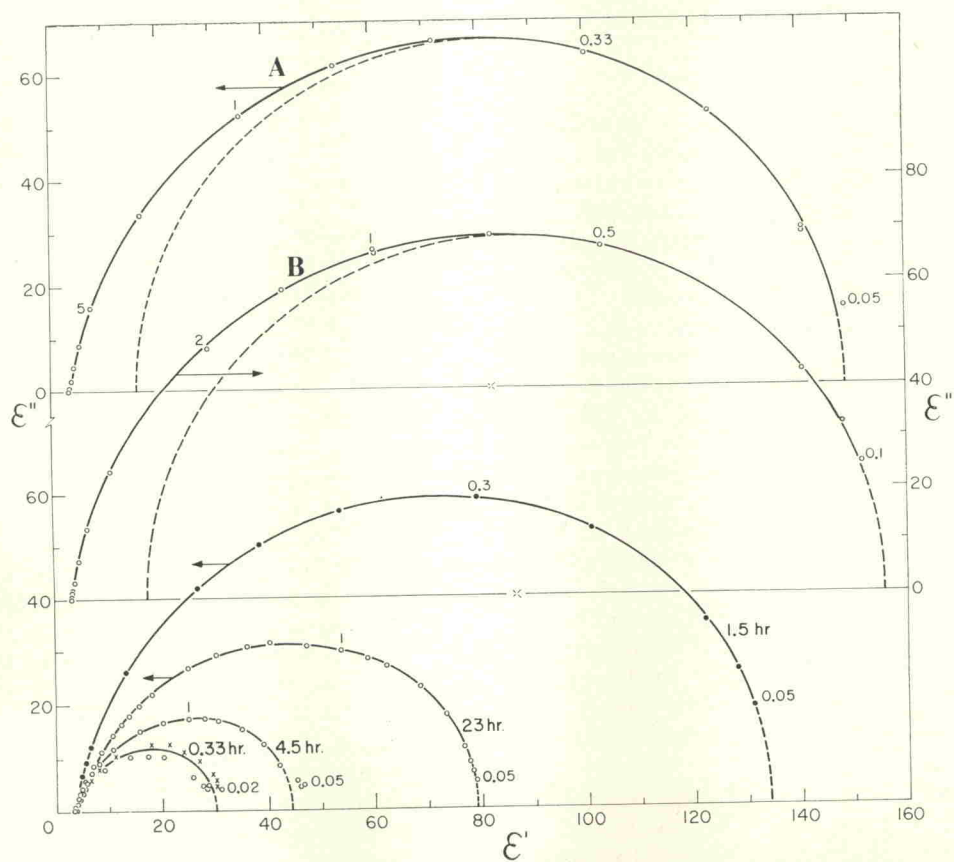


FIG. 3. Cole-Cole plots: A, cubic ice at  $-88.0^{\circ}\text{C}$  and 110 bar; B, hexagonal ice at  $-86.5^{\circ}\text{C}$  and 1 bar. The lower loci show the dispersion at various times from the start of the II $\rightarrow$ Ic transformation in the coaxial cell at  $-86^{\circ}\text{C}$ . Numbers 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  $\epsilon''$  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.<sup>22</sup> The degree of skewness varied from sample to sample; the largest value of  $\beta$  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  $\epsilon_0$ 

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  $\epsilon_0$  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<sup>1</sup> but agree quite well with the more recent data of Cole and Wörz.<sup>14</sup> 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  $T_\infty = 32^\circ\text{K}$  in the equation  $\epsilon_0 - \epsilon_\infty = A/(T - T_\infty)$ . The Cole and Wörz values were  $A = 20715$  and  $T_\infty = 38^\circ\text{K}$  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  $\epsilon_0$  over the range of temperature common to the two studies formally yield an anisotropy in  $\epsilon_0$  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  $\epsilon_0$  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  $\epsilon_0$  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.<sup>1</sup> 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