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.

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