THE ORIENTATION POLARIZATION IN HEXAGONAL ICE PARALLEL AND PERPENDICULAR TO THE *c*-AXIS

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ABSTRACT. The relative permittivity and loss of zone-refined single crystals of hexagonal ice have been measured in the temperature range 200–271 K and frequency range 0.5 Hz–0.2 MHz, using brass, stainless steel, and gold-foil electrodes. The *c*-axis of the crystal was oriented parallel to the electric field in 14 samples and perpendicular to the field in 8 samples. The equilibrium relative permittivity of orientation polarization ϵ_0, parallel and perpendicular to the *c*-axis, is 96.5 ± 1 and the average relaxation time τ_{av} is 36 μs at 265.5 ± 0.5 K; $\epsilon_0 = 124 \pm 1.5$ and $\tau_{av} = 30$ ms, at 210 K. The magnitude of the orientation polarization obeys the Curie–Weiss equation with $T_0 = 15 \pm 2$ K for both the orientations. These values are in contrast with the *c*. 17% difference in ϵ_0 for the two orientations reported in the literature. The extrapolated limiting high-frequency relative permittivity ϵ_∞, measured for both the orientations, is indistinguishable within 0.5%.

The logarithmic plot of the product of τ_{av} and temperature against the reciprocal temperature is linear in the range 210–271 K and gives an activation energy and a pre-exponential factor of 51 ± 2 kJ mol⁻¹ and 0.93 ± 0.22 ps K respectively, for both the orientations of the *c*-axis with respect to the electric field. The decrease in activation energy which has been reported to occur in polycrystalline ice and in single crystal ice near 230 K is not found until a temperature of 210 K. Single crystals of ice stored in the dielectric cell, after the completion of measurements, for periods ranging from 1–11 weeks at 253 ± 2 K showed no change in their ϵ_0, τ_{av}, ϵ_∞ that could be attributed to the effect of ageing on the orientation polarization.

RÉSUMÉ. *Polarisation de la glace Ih parallèlement et perpendiculairement à l'axe c.* La permittivité relative et le facteur de perte des cristaux de glace hexagonaux obtenus par zone fondue sont mesurés dans un domaine de température entre 200–271 K, et de fréquence comprise entre 0,5 Hz–0,2 MHz, en utilisant des feuilles électrode de laiton, d'acier et d'or. Sur 14 échantillons l'axe *c* est orienté parallèlement au champ électrique et sur 8 autres, l'axe *c* est orienté perpendiculairement. La permittivité relative en équilibre, ϵ_0, pour ces deux orientations est de 96,5 ± 1 et le temps de relaxation moyen, τ_{av}, est de 36 μs à 265,5 ± 0,5 K. A 210 K, on a $\epsilon_0 = 124 \pm 1,5$ et $\tau_{av} = 30$ ms. L'intensité de la polarisation en fonction de l'orientation obéit à l'équation de Curie–Weiss avec $T_0 = 15 \pm 2$ K pour les deux orientations. Les valeurs ϵ_0 et τ_{av} trouvées ci-dessus sont en contradiction avec celles données dans la littérature (ϵ_0 diffère de 17% entre les deux orientations). La permittivité relative extrapolée à très haute fréquence, ϵ_∞, obtenue pour les deux orientations est différente seulement de <0,5%.

Le tracé logarithmique du produit $\tau_{av}\bar{T}$, en fonction de l'inverse de la température, $1/T$, est linéaire dans le domaine de température 210–271 K. On trouve ainsi une énergie d'activation de 51 ± 2 kJ mol⁻¹ et un facteur préexponentiel de $0,93 \pm 0,22$ ps K pour les deux orientations de l'axe *c* par rapport au champ électrique. La décroissance de l'énergie d'activation aux alentours de 230 K, qui a été signalée aussi bien dans la glace polycristalline que dans le glace monocristalline n'a pu être observée même jusqu'à 210 K. Des mesures complètes de ϵ_0, τ_{av}, ϵ_∞ sur des monocristaux de glace conservés dans la cellule diélectrique pendant une période de 1 à 11 semaines à 253 ± 2 K montrent que ces valeurs restent inchangées; autrement dit, il n'y a pas eu d'influence du vieillissement quant au rôle de l'orientation de la polarisation.

ZUSAMMENFASSUNG. *Die Orientierungspolarisation in hexagonalem Eis parallel und senkrecht zur c-Achse.* Die relative Permittivität und der der dielektrische Verlust zonengereinigter Einkristalle hexagonalen Eises wurden im Temperaturbereich 200–271 K und im Frequenzbereich 0,5 Hz–0,2 MHz gemessen. Es wurden Elektroden aus Messing, rostfreiem Stahl und aus Goldfolien verwendet. Die *c*-Achse des Kristalls war in 14 Proben parallel zum elektrischen Feld gerichtet und in 8 Proben senkrecht dazu. Die relative Gleichgewichtspermittivität der Orientierungspolarisation, ϵ_0, parallel und senkrecht zur *c*-Achse, ist 96,5 ± 1 und die mittlere Relaxationszeit τ_{av} beträgt 36 μs bei 265,5 ± 0,5 K; bei 210 K ist $\epsilon_0 = 124 \pm 1,5$ und $\tau_{av} = 30$ ms. Der Betrag der Orientierungspolarisation folgt einer Curie–Weiss-Gleichung mit $T_0 = 15 \pm 2$ K für beide Kristallrichtungen. Diese Werte stehen im Gegensatz zu den etwa 17% Unterschied in ϵ_0 für die beiden Kristallrichtungen, die in der Literatur angegeben werden. Der extrapolierte Hochfrequenzgrenzwert der relativen Permittivität, ϵ_∞, gemessen in beiden Kristallrichtungen, ist innerhalb 0,5% nicht unterscheidbar.

Das logarithmische Diagramm des Produkts von τ_{av} und der Temperatur in Abhängigkeit der reziproken Temperatur ist im Bereich 210–271 K linear und gibt eine Aktivierungsenergie von 51 ± 2 kJ mol⁻¹ und einen Exponentialvorfaktor von $0,93 \pm 0,22$ ps K für beide Richtungen der *c*-Achse in bezug zum elektrischen Feld. Eine Abnahme der Aktivierungsenergie, die in vielkristallinem und einkristallinem Eis nahe bei 230 K eintreten soll, wurde bis herab zur Temperatur von 210 K nicht gefunden. Eis-Einkristalle, die nach der Beendigung der Messungen in der dielektrischen Messzelle für Zeitdauern von 1–11 Wochen bei 253 ± 2 K gelagert wurden, zeigten in ihren ϵ_0, τ_{av} und ϵ_∞ keine Veränderung, die einem Alterungseinfluss auf die Orientierungspolarisation zugeordnet werden könnte.

1. INTRODUCTION

It has been held generally that the limiting low-frequency relative permittivity of orientation polarization ϵ_0 of hexagonal ice is higher along the c-axis than along the a- or b-axis. While most workers accept that some difference in ϵ_0 along the various axes, which may possibly be caused by the non-equivalence between the energy of the six orientations of a water molecule in ice, might exist at very low temperatures, a controversy remains over the magnitude of the difference at relatively high temperatures.

Humbel and others (1953), who first measured the dielectric properties of single crystals of ice, stated: "The relative difference $(\epsilon_c - \epsilon_{\perp c})/\epsilon_c$ at 1 kc/sec is about 15% at $-5°C$, about 12% at $-20°C$ and about 8% at $-40°C$". Here ϵ_c and $\epsilon_{\perp c}$ represent the relative permittivity along and perpendicular to the c-axis, respectively. The difference persisted at lower frequencies, and at 252.6 K the difference between ϵ_0 parallel and perpendicular to the c-axis, was 19. Wörz and Cole (1969), who measured the ϵ_0 of zone-refined single crystals of ice parallel and perpendicular to the c-axis, stated their finding: ". . . the data [parallel to the c-axis] are less reliable but indicate little if any anisotropy of the static dielectric constant near the melting point, rather than a difference of the order of 10% reported by Humbel, Jona and Scherrer". Here, the "static dielectric constant" refers to ϵ_0.

The contribution to the relative permittivity from orientation polarization, $\Delta\epsilon$ ($= \epsilon_0 - \epsilon_\infty$, where ϵ_∞ is the limiting high-frequency relative permittivity), in Von Hippel and others' (1971) results at 253 ± 0.1 K for five ice samples measured parallel to the c-axis, varied from 99.8 to 112.6 and for two samples measured perpendicular to the c-axis, from 78.8 to 96.4. At 194.4 ± 0.3 K, the $\Delta\epsilon$ for the same five samples parallel to the c-axis varied from 192 to 243. From an analysis of their data for various samples, Von Hippel and others (1971) concluded: "With the electric field parallel to the optic axis ($E\|c$), our best measurements give $\Delta k_3 = 112.3$ at $-20°C$ compared to 96.3 for $E\perp c$. Thus, as to the degree of anisotropy, we are closer to the early data of Humbel, Jona, and Scherrer than Cole–Wörz". In Von Hippel and others' (1971) notation, $\Delta k_3 \approx \Delta\epsilon$. Ruepp (1973), who studied zone-refined single crystals of ice in the frequency range 0.5 mHz–100 kHz and temperature range 103–273 K, stated his conclusion: "An anisotropy of $\epsilon_s - \epsilon_\infty$ is possible but it cannot be derived from these [Ruepp's] results". In Ruepp's (1973) notation, $(\epsilon_s - \epsilon_\infty) = \Delta\epsilon$.

Taubenberger (1973) reported that a sample of ice measured with evaporated gold electrodes and kept for 1 850 h had $\Delta\epsilon_{\perp c} = 89.0$ at 258 K. Another sample at the same temperature but kept for 1 140 h had $\Delta\epsilon_{\|c} = 106.5$. Thus there is a difference of 17.5 between the $\Delta\epsilon$ measured parallel and perpendicular to the c-axis at 258 K, which difference is the same as interpolated from Humbel and others' (1953) data. Maeno (1973) measured one sample of ice at 246.7 K using stainless steel electrodes and reported his finding: "In fig. 27.a, curve A shows the frequency characteristics of dielectric constant of pure ice ($c\|$), in which dispersion occurs only in a frequency range from 10^2 Hz to 5×10^4 Hz and the dielectric constant has a constant value of 110 at lower frequencies". The corresponding value interpolated from Humbel and others' (1953) data is 120.

The theoretical treatment of the orientation polarization within the constraints of the Bernal–Fowler rules (Bernal and Fowler, 1933), and the residual entropy of ice of 3.41 ± 0.22 J K^{-1} mol^{-1} (Haida and others, 1974), also seems to remain inconclusive on a possible anisotropy of ϵ_0. Nagle (1974) in his series expansions of dipolar correlations, which expansions are somewhat different from the ones used by Gobush and Hoeve (1972) and Stillinger and Cotter (1973), stated, "Our series expansions confirm that the anisotropy in ϵ_0 is indeed small for the BFP (Bernal–Fowler–Pauling) model. It is now up to the experimentalists to reach agreement on the actual anisotropy". However, Nagle (1974) considers it also possible to explain theoretically a fairly large anisotropy of orientation polarization that would be compatible with the uncertainty of ± 0.22 J K^{-1} mol^{-1} in the present value of the residual

entropy of ice. In such a case the Pauling–Slater–Takagi–Bethe type approximation (Nagle, 1974) would need to be made to obtain the ϵ_0 of ice parallel and perpendicular to the c-axis.

The purpose of this study was to measure accurately the dielectric properties of single crystals of ice with the electric field oriented (i) parallel and, (ii) perpendicular to, the c-axis over a frequency and temperature range where reliable values of ϵ_0 could be obtained. This paper reports the results of the measurements.

2. Experimental methods

2.1. *The electrical equipment*

The equipment used for measurement of capacitance and conductance of ice in the frequency range 0.5 Hz to 0.2 MHz has been described elsewhere (Johari and Jones, 1976[a]). The calibration of the instruments was regularly checked to ensure the accuracy of the data which is the same in the present results as in the earlier (Johari and Jones, 1976[a]).

2.2. *The dielectric cells*

All electrical measurements were carried out on disc-shaped ice samples contained in three-terminal dielectric cells with guarded parallel-plate electrodes. One set of electrodes was made of brass and two of stainless steel. For measurements on three samples of ice, two parallel to the c-axis and one perpendicular to the c-axis, the stainless steel electrodes E and K of the cell shown in Figure 1 and described below, were covered with gold foil c. 1 μm thick.

Three dielectric cells were used in this study. Two of the dielectric cells, one made of brass and the other of stainless steel, were made to a design similar to McCammon and Work's (1965). This is shown in Figure 1. The 12.7 mm thick, 152 mm diameter, plates A and J, and the four 12.7 mm thick rods C threaded at both ends form a yoke, the top plate of which had a concentric bore of 12.7 mm diameter. The high electrode E, 65 mm in diameter and
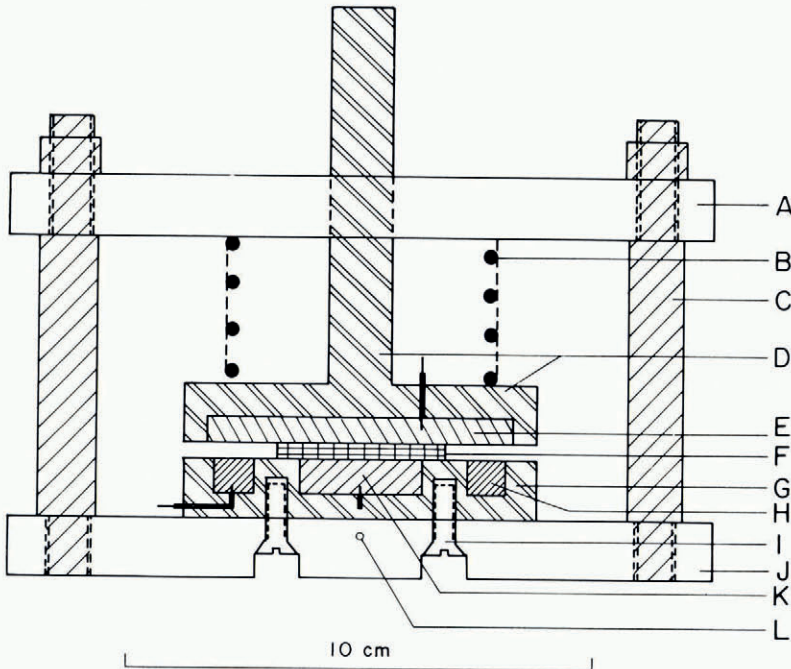

Fig. 1. *Diagram of the dielectric cell used for the study of single crystals of ice.*

7 mm thick, was embedded inside a groove cut out from an inverted mushroom-shaped ground electrode D, whose stem was 12.7 mm in diameter and 82 mm long. The lubricated stem slid through the bore in plate A with a clearance of 12.7 μm. The low electrode K, 25.4 mm in diameter and 7 mm thick, was embedded in a concentric groove cut out from the disc G, which also received another concentric low electrode H shaped in the form of a ring, 62 mm in outer and 44 mm in inner diameter and 7 mm thick. K and H were 10 mm apart. G was permanently fixed to the plate J by means of four screws I, as shown in Figure 1. A 2 mm diameter hole L was drilled in the plate J from the circumference to the centre of the plate to receive a thermocouple. B is a stainless steel spring which maintained an axial load of 15–20 kg on a plate 5 mm thick inserted between E and K and thus ensured contact between the ice and electrodes at the various temperatures. The electrodes E, H, and K were electrically insulated from the ground electrodes D and G by means of mica and water-repellant epoxy cement, and the assemblies DE and GHK were honed to a smooth finish and their faces lapped flat and parallel. The gaps between the guard rings and the electrodes E, H, and K were between 0.5–0.8 mm. The width of the guard planes were two to three times the thickness of the ice sample F to provide negligible fringing of the electric field. Measurement of ϵ_0 of n-hexane with this cell showed a stray capacitance of less than 0.1%.

The cell has the advantage of measuring the dielectric properties of a sample without explicit knowledge of the sample thickness. When D and G are parallel, the effective air capacitance between E and H and E and K is given by

$$C_K/C_H = A_K/A_H,$$

where C_K and C_H are the effective air capacitance and A_K and A_H are the area of the electrodes K and H, respectively. The factor (A_K/A_H) was determined by placing stainless steel rings between D and G which provided an electrode separation in the range 3–7 mm. The value was 2.893 6 for brass electrodes and 2.907 9 for stainless steel electrodes. The values increased by c. 2×10^{-4} when the temperature was decreased from 295 K to 223 K due to a combined effect of a decrease in the area of the electrodes, K and H and in the thickness of the steel ring. The air capacitance of an assembly containing a sample of unknown thickness placed on K can thus be obtained by measuring C_H. Since the top electrode E is supported by the specimen F, the cell has the further advantage of measuring the isobaric expansivity of materials from a knowledge of the change in C_H with temperature (McCammon and Work, 1965).

A third parallel-plate cell made of stainless steel, which was the model Type KMT Guard-ring Capacitor, was commercially available from Rohde and Schwarz, W. Germany. It consisted of an 80.3 mm diameter low electrode protected by a guard ring. The spacing between the high and low electrodes could be varied up to 9 mm by means of a micrometer. The gap between the low and the guard electrode was 0.4 mm. The cell has been designed such that an axial load of 8 kg can be applied to the electrodes in order to maintain an appropriate electrical contact with the sample. For a sample thickness of 6 mm, the cell has an air capacitance of 7.62 pF and a stray capacitance of 0.14 pF. The permittivity and loss measured with the cell were corrected for the stray capacitance.

The temperature was measured by means of a calibrated copper–constantan thermo-couple which was kept inside the hole L in plate J shown in Figure 1. The thermocouple was placed under the low electrode in the Type KMT Capacitor. In order to ascertain that the temperature between the plates E and K was the same as inside plate J, a thermocouple embedded in felt material 8 mm thick was kept between E and K. No difference between the temperature of the two thermocouples was detected in the range 200–295 K.

2.3. *The ice samples and their preparation*

The single crystals of ice were prepared from distilled water contained in polyethylene tubes of 10 cm internal diameter and 1.1 m long, by zone-refining in a cold room maintained

at 263 ± 1 K. The treatment of water, the number of passes made during the zone refining, the age of single crystals prior to the study, and the number of samples studied for each orientation are given in Table I.

TABLE I. PREPARATION AND DESCRIPTION OF THE ICE CRYSTALS OBTAINED BY ZONE-REFINING METHOD, AND DETAILS OF THE SAMPLES AND ELECTRODES USED IN THE STUDY

Laboratory label	Treatment of water	Number of passes	Duration of the passes months	Age of the crystal at the time of study years	Number of samples measured parallel to the c-axis and the electrodes used	Number of samples measured perpendicular to the c-axis and the electrodes used
D1	de-ionized and boiled	1	3	2.3 ± 0.2	1 (gold); 2 (steel)	1 (brass)
D2	de-ionized and boiled	2	5	1.5 ± 0.2	1 (brass); 1 (steel)	1 (steel); 1 (gold)
MP1	millipore filtered	1	4	1.2 ± 0.3	2 (brass); 1 (gold)	1 (brass); 2 (steel)†
DF1	millipore filtered, de-ionized and boiled	3	9	2.0 ± 0.2	1 (brass); 1 (steel)†	1 (steel)†
DF2	millipore filtered and de-ionized	3	10	1.8 ± 0.3	2 (steel)	
ZR1*	de-ionized	1	3	8 ± 1	1 (brass)	
ZR2*	de-ionized	1	3	8 ± 1	1 (steel)	1 (brass)

* Prepared by Dr R. O. Ramseier at the U.S. Cold Regions Research and Engineering Laboratory, Hanover, N.H., U.S.A.
† Samples studied with Type KMT Capacitor.

The crystallographic axis of the 60–70 mm thick cylindrical sample of ice was first determined using crossed polarizing filters. In nearly all crystals the c-axis lay perpendicular to the cylindrical axis of the single crystals. The cylindrical sample was then cut with a band saw to machinable dimensions with a suitably oriented c-axis. Finally, the discs of ice from different stocks, 3–6 mm in thickness and 28–30 mm in diameter, were cut on a lathe. Disc samples of the same diameter but c. 2 mm thickness were also cut from the same stock, and at least one sample from each stock was used for accurately determining the direction of the c-axis by means of X-ray diffraction, prior to making the electrical measurements. The X-ray measurements showed that the c-axis of the disc sample lay within 0.5–2° of the desired direction. Two samples were also examined by X-ray diffraction after they had been taken out of the dielectric cell to ensure that the c-axis orientation had not altered, and nearly all samples were examined after the completion of electrical measurements with crossed polarizing filters to ensure the single crystallinity of the ice. No change in the c-axis orientation or in crystallinity was found in samples which were stored in the dielectric cell for as long as two months at 258 ± 2 K under a uniaxial stress.

The ice samples used with the Type KMT Capacitor were 85–90 mm in diameter and c. 6 mm in thickness. Two samples with the c-axis perpendicular to the electric field and one sample with the c-axis parallel to the electric field were studied with this capacitor and the rest of the samples were studied with the cell shown in Figure 1.

The dielectric cell containing the ice sample was placed in a polyethylene bag, the leads were taken out and the bag closed. The entire assembly was kept inside a thermostatically air-cooled refrigeration unit capable of cooling to a temperature of 199 K. In several experiments, two cells containing the ice samples, having either the same or different c-axis orientations, were kept in the cold chamber. Measurements could thus be made on several samples at identical temperatures after thermal equilibrium was reached. The temperature of the cells

remained constant to within ± 0.05 K for 2–3 h. Therefore, there is little uncertainty in the values derived from our measurements of capacitance and conductance, which might otherwise exist from any variation in the temperature of the ice sample during the period of the frequency scan.

3. Sources of error

In order to ascertain the reliability of our results, it is important to discuss the possible errors in our measurements, and the consequent effect of such errors on the quantities derived. An error in the air capacitance C_K corresponding to a given thickness of the ice sample contained in an enclosed dielectric cell, may be caused if the ice sublimed and redeposited on the faces H and E in Figure 1. Since C_K is calculated from the ratio (A_K/A_H) and the value of C_H, both measured in air, an increase in C_H caused by a thin deposit of ice on H and E would give an apparently high value of C_K and consequently a low value of the relative permittivity and loss. A sample of ice was kept in the dielectric cell enclosed in a polyethylene bag and C_H was measured with time. No increase in C_H was found over a period of seven weeks. So, the errors due to a possible sublimation of ice are too small to be detectable.

A major error in the value of ϵ_0 would be caused by the air gap between ice and the electrodes if the faces of the ice sample were not flat and parallel, or if one or both faces were convex. Although annealing of ice under a load of 15–20 kg at 268 K for 4–5 d may sufficiently deform the ice and thus reduce the air gaps, it was necessary to ensure that such an air gap did not exist. Therefore, after measurements on a sample of ice had been made at a few temperatures, the dielectric cell containing the ice was immersed in n-hexane at 268 K, and measurement of capacitance and conductance made again at several frequencies between 0.1–5 kHz. If immersion of the dielectric cell in n-hexane caused an increase in the measured values of capacitance and conductance, the ice sample and all the data obtained on it were rejected. The data given here are only for those samples whose values of capacitance and conductance remained unaltered when the ice was surrounded by n-hexane.

Air between the ice and electrodes can also be entrapped if the faces of the discs of ice are concave. Such air gaps cannot be detected by the above procedure, because ice around the air gap would seal the gap from the outside. This may also cause a significant error in our data. From Davidson and Wilson's (1963) formulae for the effect of air gaps on the dielectric properties, we calculate that a uniform air gap of 1 μm for a 5 mm thick sample of ice would give values of ϵ_0 and relaxation time 2% lower, and of ϵ_∞ 0.07% lower, than the true values. It is conceivable that an air gap of < 1 μm could exist in some of our assembled electrodes containing ice, although our experience with the reproducibility of 1% in the ϵ_0 values for the same sample of ice, suggests that the error due to such an air gap is indistinguishable from the overall errors in the estimate of ϵ_0. Furthermore, since an error due to the presence of such an air gap, could occur with equal probability in samples of both the orientations, we feel certain that such an error would not affect our conclusions concerning the anisotropy of ϵ_0 in ice.

Possible errors in the capacitance and conductance measurement have already been discussed (Johari and Jones, 1976[a]) and those in the temperature were given in the preceding section. Errors due to both sources are less than 0.2% in ϵ_0.

4. Results and discussion

4.1. *The frequency dependence of ϵ' and ϵ''*

The relative permittivity ϵ' and loss ϵ'' of ice, measured within 2 h of sample preparation, exceeded 250 and 200, respectively at 0.1 kHz and 268 K. The values decreased rapidly with time and a typical complex-plane plot of ϵ'' against ϵ' followed the pattern indicated in Figure 2. In nearly all cases, ϵ'' decreased to a value of 4 or lower at 268 K in 60–80 h.
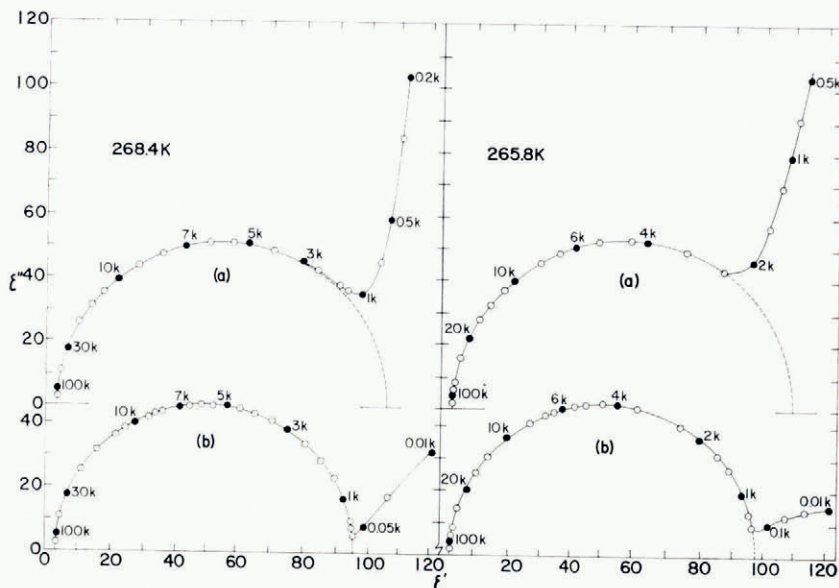
Fig. 2. The change in the shape of the complex-plane plots of the relative permittivity and loss of an ice sample measured paralle to the c-axis. Left half: measured at 268.4 K, (a) after 48 h, (b) after 70 h. Right half: measured at 265.8 K, (a) after 49 h, (b) after the application of 2.1 kV cm⁻¹ electric field along the c-axis for 1.8 h. The numbers besides the filled data points are frequencies in hertz.

Measurements at low temperatures were made only after the value of ϵ'' at 0.1 kHz was less than 4 at 268 K. In most cases, after the completion of the low-temperature measurement, which took 4–8 d, the sample when measured again at 0.1 kHz had $\epsilon'' < 3$ at 268 K. The annealing of the ice was found to be most effective in reducing its ϵ'' to a limiting value when done at temperatures close to 270 K. Therefore, all ice samples were stored in a cold room maintained at 268 ± 1 K, when not being measured. A similar observation was reported by Taubenberger (1973).

The ϵ'' of ice at 0.1 kHz and 266 K was also found to decrease when an electric field of c. 2 kV cm⁻¹ was applied for 1–2 h. After removal of the field the value of ϵ'' remained constant for nearly 10 min and then began to increase with time. The behaviour, which seems typical of ice (Gränicher and others, 1955; Von Hippel and others, 1971) and of clathrate hydrates (Wilson and Davidson, 1963; Davidson and Wilson, 1963), is shown in Figure 2. While the application of a d.c. voltage for a period of 2 h sufficiently reduced the ϵ'' of ice to obtain reliable values of its ϵ_0, the increase in ϵ'' with time after removal of the field made the measurements somewhat uncertain. The reduction in ϵ'' at low frequencies on the application of a d.c. voltage suggests that slow build-up of space charge, arising either from the irreversibility of the electrode material to protons, or from the presence of ions (Davidson and Wilson, 1963) in ice, is responsible for higher values of ϵ'' than anticipated from the orientation polarization alone.

The ϵ' and ϵ'' of ice are plotted in a complex plane at several temperatures in Figure 3. In the temperature range of study both the low- and high-frequency part of the arc could be well defined, and, as evident in Figure 3, the plots intersect the ϵ' axis very nearly vertically. With decreasing temperature, the plots depart progressively from a semicircle, although for temperatures above 250 K the plots are semicircular and are indistinguishable from a Debye-type process with a single relaxation time. This feature is clearly seen in Figure 4 in which the
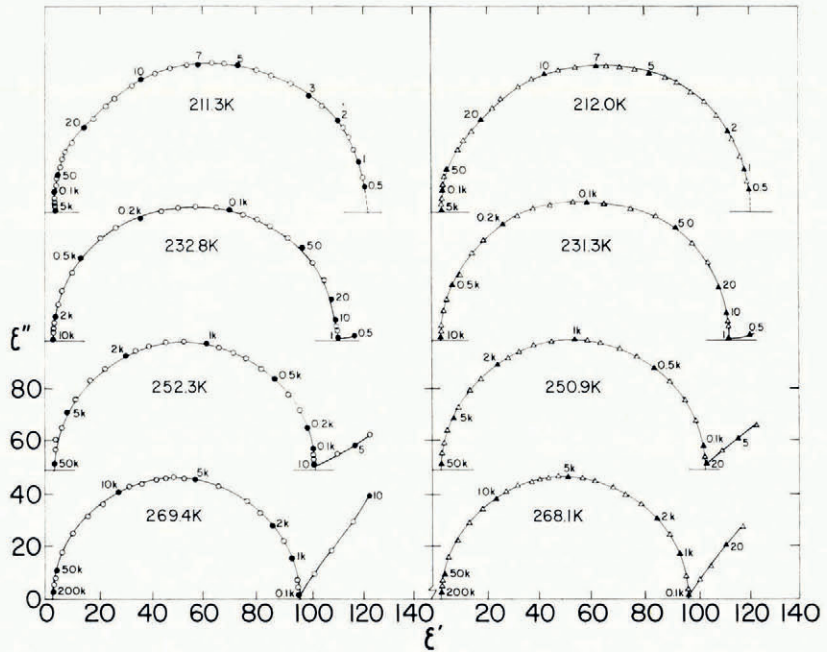
Fig. 3. Complex-plane plots of the relative permittivity and loss of ice at several temperatures. The left half is for measurement with the c-axis oriented parallel to the electric field and the right half for that oriented perpendicular to the field. The numbers besides the filled data points are frequencies in hertz. The plots have been progressively shifted upwards as indicated by the axis.
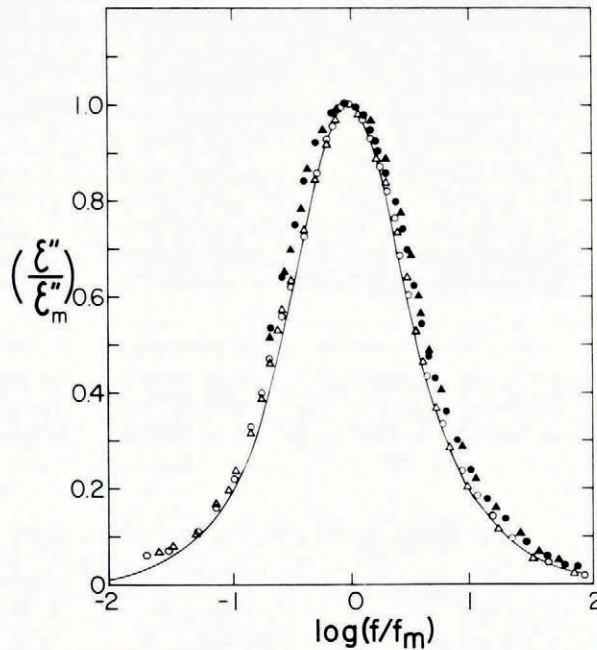

Fig. 4. Normalized plots of the dielectric loss of ice against frequency at several temperatures. The solid line is the theoretical curve for a Debye-type relaxation. ○, parallel to the c-axis at 238.1 K and ●, at 201.5 K. △, perpendicular to the c-axis at 235.9 K and ▲, at 202.6 K.

normalized dielectric loss ϵ''/ϵ''_m of one sample of ice of each orientation is plotted against f/f_m on a logarithmic scale. Here ϵ_m'' is the maximum loss and f_m the frequency of maximum loss. The solid line represents a Debye-type absorption with a single relaxation time.

The half-width of the normalized plots at temperatures <230 K varied from one sample to another. Therefore, no further analysis of the frequency dependence of ϵ' and ϵ'' into several dispersion regions was attempted. The ambiguity of such an analysis has already been discussed in the literature (Gough and others, 1973; Johari and Jones, 1976) and it is not certain whether the increase in the half-width of the plots with decreasing temperatures is due to an increase in the relative amplitude of several Debye-type relaxations or to an increase in the relative magnitude of the limits of relaxation time representing a distribution. At temperatures near 205 K, the approach of ϵ'' towards the axis at high frequencies indicated the presence of a small relaxation region, similar to the one seen in D_2O ice (Johari and Jones, 1976). A similar high-frequency relaxation region has also been observed in H_2O ice single crystals by Von Hippel and others (1971), and Ruepp (1973) at kilohertz frequencies but a temperatures below 240 K and 200 K, respectively, and by Johari (1976) at megahertz frequencies at temperatures above 250 K.

4.2. *The equilibrium relative permittivity*

The equilibrium relative permittivity ϵ_0 was obtained from a graphical extrapolation of the low-frequency end of 86 plots for samples with the c-axis oriented parallel to the electric field and 61 plots for samples with the c-axis oriented perpendicular to the electric fields. Strictly, $\epsilon' = \epsilon_0$, when $\epsilon'' = 0$. For ice, and for many other solids, this condition is not observed because space-charge and other non-linear polarizations begin to contribute to ϵ' at frequencies far above the one at which ϵ'' due to orientation polarization would become zero. Within the reproducibility of $\pm 2\%$, our values of ϵ_0 are not likely to be different from the
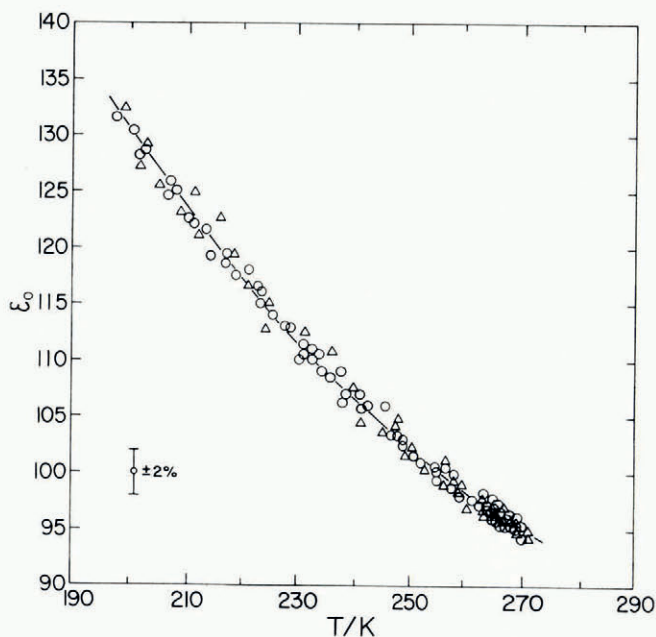

Fig. 5. *The variation of the equilibrium relative permittivity of ice with temperature;* ○, *parallel to the c-axis;* △, *perpendicular to the c-axis.*

TABLE II. EQUILIBRIUM RELATIVE PERMITTIVITY AND RELAXATION TIME OF
HEXAGONAL ICE NEAR 266 K FOR THE TWO ORIENTATIONS

Orientation of the ice crystal within $\pm 2°$	Temperature K	ϵ_0	τ_{av} μs
c-axis parallel to the electric field	265.9	96.8	35.5
	265.6	96.3	36.5
	265.9	96.9	36.4
	266.1	95.7	36.8
	265.4	96.9	38.0
c-axis perpendicular to the electric field	265.9	96.3	35.8
	265.1	95.8	35.0
	265.8	96.1	36.2
	265.7	96.3	36.2
	265.7	95.8	35.1

true ϵ_0, although the condition $\epsilon'' = 0$ was not satisfied by any set of our measurements. The ϵ_0 of ice for both the orientations is plotted in Figure 5, and values near 266 K for five different samples are given in Table II.

The ϵ_0 measured parallel to the c-axis at 248 K and 268 K are 103 and 96 respectively. The corresponding values interpolated from Humbel and others (1953) are 120 and 113, from Von Hippel and others (1971) are 118 and 106, and from Taubenberger (1973) for his B14 sample are 113 and 106. Thus there is a considerable difference between our ϵ_0 measured parallel to the c-axis and those given in the literature. While the scatter in ϵ_0 values, already mentioned in Section 1, in Von Hippel and others' (1971) data, may account for some degree of difference, the reasons for a difference between our data and those of Humbel and others (1953) and Taubenberger (1973) are not obvious. Our values agree with Wörz and Cole's (1969) values in which the errors in ϵ_0 from space-charge polarization and "d.c. conductivity" were largely eliminated.

The value of $\epsilon_0 = 96$, measured perpendicular to the c-axis at 268 K, agrees with the values reported by Humbel and others (1953), by Wörz and Cole (1969), by Von Hippel and others (1971) and by Taubenberger (1973), within their respective uncertainty, which Humbel and others (1953) quoted for their ϵ' values, ". . . ist deshalb von der Grössenordnung 3,5–4,5%".

For a given sample of ice, our ϵ_0 values showed a scatter from a mean line of less than $\pm 0.7\%$. The scatter increased when ϵ_0 of several different samples was plotted on the same figure. In all cases of 14 samples measured parallel to the c-axis and 8 measured perpendicular to the c-axis, the departure of the data from a mean line did not exceed 2%, as indicated in Figure 5. We attribute the apparent uncertainty in ϵ_0 to the possible non-parallel faces of the sample, as discussed in Section 3, or the nature of ice itself. Within this uncertainty, the ϵ_0 measured parallel to the c-axis is the same as that measured perpendicular to the c-axis as the data in Table II and Figure 5 indicate.

The ϵ_0 values were fitted to the Curie–Weiss equation,

$$\epsilon_0 - \epsilon_\infty = \frac{A}{T - T_0}, \tag{1}$$

where ϵ_∞ is the limiting high-frequency permittivity of the orientation polarization, T is the absolute temperature, and A and T_0 are empirical constants. The values of A and T_0 obtained, assuming $\epsilon_\infty = 3.2$, for ice for the two orientations and for all samples and orientations, are given in Table III, and a plot of $(\epsilon_0 - \epsilon_\infty)^{-1}$ against temperature is shown in Figure 6. The standard deviation of A and T_0 and of the data points obtained from a least-square treatment are also included. The agreement between A and T_0 for the two orientations indicates the consistency of our measured values for different samples. Our A and T_0 values in Table III

differ from those given by Wörz and Cole (1969), who found $A = 20\,715$ K and $T_0 = 38$ K, and from those obtained from Von Hippel and others' (1971) plots, where the values of A for the two orientations differ considerably, but the T_0s are close to o K. The values of A and T_0 are very sensitive to changes in the input data, and probably have little significance except for the purpose of interpolation.
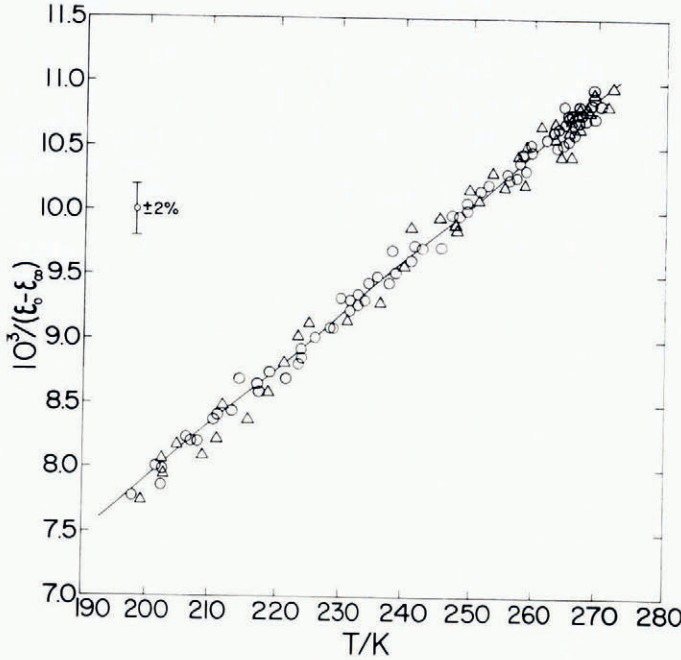

Fig. 6. *The variation of* $(\epsilon_0 - \epsilon_\infty)^{-1}$ *with temperature for ice;* ○, *parallel to the c-axis;* △, *perpendicular to the c-axis.*

TABLE III. THE EMPIRICAL CONSTANTS OF THE CURIE–WEISS EQUATION, AND THE PRE-EXPONENTIAL FACTOR AND ACTIVATION ENERGY CALCULATED FROM EYRING'S EQUATION FOR HEXAGONAL ICE FOR THE TWO ORIENTATIONS

Orientation	A K	T_0 K	Standard deviation $\times 10^{-1}$	τ_0 ps K	$E^\star$ kJ mol^{-1}	Standard deviation
c-axis parallel to the electric field	$23\,490 \pm 200$	14 ± 2	0.69	2.3 ± 3.4	49.4 ± 2.5	0.33
c-axis perpendicular to the electric field	$23\,260 \pm 400$	16 ± 4	1.10	0.23 ± 0.14	53.9 ± 0.8	0.08
combined data for both orientations	$23\,400 \pm 200$	15 ± 2	0.87	0.93 ± 0.22	51.1 ± 1.6	0.27

The uncertainty in A, T_0, τ_0, and $E^\star$ is the standard error from a least-square fit of the data plotted as in Figures 6 and 8. The standard deviation also refers to the relevant plots.

From the recent discussion (Hollins, 1964; Rahman and Stillinger, 1972; Gobush and Hoeve, 1972; Stillinger and Cotter, 1973; Nagle, 1974) of the theoretical treatment of the orientation polarization in ice, there is little agreement between the various workers on the choice of dipolar interactions that affect the ϵ_0 of ice. Consequently, it is not certain whether the short-range interactions, within the constraints of Bernal–Fowler rules (Bernal and Fowler, 1933) and Pauling's (1935) calculation of residual entropy, used by Onsager and Dupuis (1962) and later by Nagle (1974), should be used in calculating the ϵ_0, or whether the long-range interactions as in Kirkwood's theory (1940) for solids, or only short-range interactions, as in Kirkwood's theory (1939) for liquids, would be more appropriate.

Nagle (1974) has proposed that ϵ_0 of ice is likely to be isotropic, on the theoretical grounds mentioned above, and the equation of Onsager and Dupuis (1962) can be written in the form:

$$\epsilon_0 - \epsilon_\infty = 4\pi N \mu^2 G / 3 V k T, \tag{2}$$

where G is defined as the polarization factor, N is Avogadro's number, μ is the dipole moment of a water molecule in ice, V is the molar volume, k is the Boltzmann factor, and T is the temperature. Nagle (1974) calculated $G = 3$. The Kirkwood–Fröhlich (Fröhlich, 1949) equation, which takes account of short-range interactions, is

$$\epsilon_0 - \epsilon_\infty = [3\epsilon_0/(2\epsilon_0 + \epsilon_\infty)](4\pi N m^2 \mu_0^2 g / 3 V k T), \tag{3}$$

where g is the orientational correlation factor, which is a measure of the extent to which hindered rotation of neighbouring molecules tends to align their dipolar orientations, m is a measure of the enhancement of the dipole moment by its own reaction field, and μ_0 is the dipole moment of a water molecule in the vapour state, according to Clough and others (1973), $\mu_0 = 1.855$.

From a comparison of Equations (2) and (3), G and g are formally related by,

$$\mu^2 G = [3\epsilon_0/(2\epsilon_0 + \epsilon_\infty)] m^2 \mu_0^2 g. \tag{4}$$

Since $\epsilon_0 \gg \epsilon_\infty$ for ice, Equation (4) becomes

$$\mu^2 G = 1.5 m^2 \mu_0^2 g. \tag{5}$$

In contrast to μ_0, μ is not accessible to direct measurement. It is noteworthy that if $g = 2.07$ (Rahman and Stillinger, 1972) and $G = 3$ (Nagle, 1974) are substituted in Equation (4), μ becomes approximately equal to $m\mu_0$. From Equation (2) the dipole moment of a water molecule $\mu = 2.97 \times 10^{-18}$ e.s.u. at 243.1 K, which gives the charge associated with a Bjerrum defect (Bjerrum, 1951), $q = 1.87 \times 10^{-10}$ e.s.u. (6.25×10^{-20} C). This value is close to that estimated by Onsager and Dupuis (1962).

In Equation (3), m is given by either $(\epsilon_\infty + 2)/3$ or $(n^2 + 2)/3$, where n is the refractive index at optical frequencies. There has been a considerable discussion (Hollins, 1964; Chan and others, 1965; Johari and Jones, 1976) as to which of the two quantities ϵ_∞ or n^2 is appropriate in the calculation of m and some ambiguity still remains as to the frequency at which the orientation polarization separates from the distortion polarization. From Figures 5 and 7
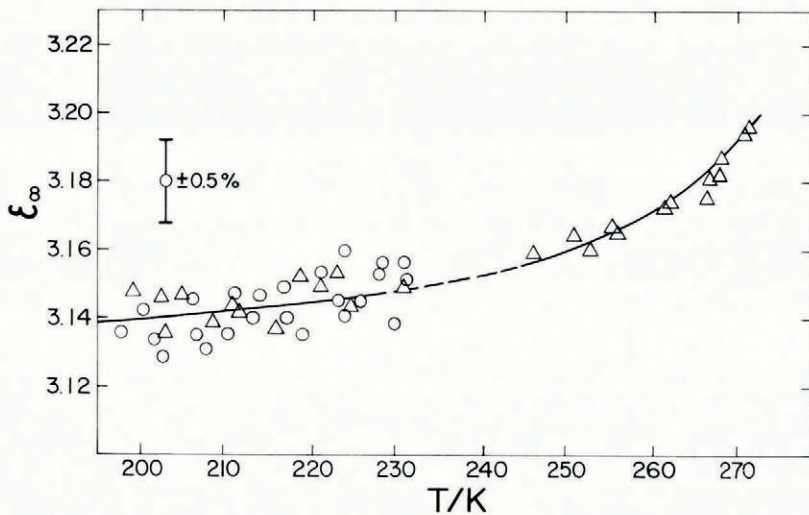

Fig. 7. The limiting high-frequency relative permittivity plotted against temperature; $\bigcirc$, parallel to the c-axis, and $\triangle$, perpendicular to the c-axis. The data points above 240 K are from Johari (1976).

$\epsilon_0 = 105.2$ and $\epsilon_\infty = 3.15$ for both the orientations in ice at 243 K. Using Equation (3), one obtains $g = 1.78$, if $m = (\epsilon_\infty+2)/3$, and $g = 3.40$, if $m = (n_D^2+2)/3$ using the refractive index n_D for sodium D light. Evidently the g calculated assuming $m = (\epsilon_\infty+2)/3$ is close to the theoretical value of 2.07 calculated by Rahman and Stillinger (1972) for ice containing 2 048 molecules using a Monte-Carlo procedure. We have arrived at a similar conclusion from a somewhat different consideration in the case of D_2O ice (Johari and Jones, 1976[b]).

Another consideration concerning the choice between ϵ_∞ and n^2 in calculating m would be useful here. If the $(\epsilon_0-\epsilon_\infty)$ of ice obeyed Curie's law, i.e. if $T_0 = 0$ K in Equation (1), as Ruepp and Käss (1969), Von Hippel and others (1971), Ruepp (1973), and Johari and Whalley (1973) have found, a comparison of Equation (1) with Equation (2) gives

$$A = 4\pi N\mu^2 G/3Vk \qquad \text{(if } T_0 = 0 \text{ K).} \qquad (6)$$

Since $\epsilon_0 \gg \epsilon_\infty$ for ice, the first term on the right-hand side of Equation (3) becomes 1.5, and then from a comparison of Equations (1) and (3),

$$A = 2\pi Nm^2\mu_0^2g/Vk \qquad \text{(if } T_0 = 0 \text{ K).} \qquad (7)$$

The molar volume of ice, V, decreases from 19.66 cm³ mol⁻¹ at 273 K to 19.45 cm³ mol⁻¹ at 200 K (Lonsdale, 1958) and G and g remain constant. It follows, then, that A can be constant only if μ^2 and m^2, in Equations (6) and (7) respectively, decrease with temperature in the same proportion as the molar volume. Such a decrease in μ^2 is implicit in Equations (2) and (6), via the temperature dependence of the O—O distance d, which determines the charge q associated with a Bjerrum defect by $q = 3^{\frac{1}{2}}\mu/d$, if q is assumed to remain constant with temperature. The decrease in O—O distance corresponding to the above-mentioned decrease in V is from 2.76 Å at 273 K to 2.75 Å at 200 K (Lonsdale, 1958).

The term m in Equations (3) and (7) is temperature dependent via the temperature dependence of ϵ_∞ or n_D^2. As the n_D^2 of ice calculated from Clausius and Mossotti's relation *increases* (Johari, 1976) from 1.715 at 273 K to 1.724 at 200 K, but ϵ_∞ decreases from 3.20 to 3.14 (Fig. 7) in the same temperature range, it is apparent that m should be given by either $(\epsilon_\infty+2)/3$, or else a quantity that decreases with temperature, if A in Equation (7) were to remain constant.

4.3. *The limiting high-frequency relative permittivity*

The values of ϵ_∞ were obtained by a graphical extrapolation of the high-frequency end of the complex-plane plots of ϵ' and ϵ''. Reliable values could be obtained only at temperatures where ϵ'' at 100 kHz was less than 0.1. This condition was satisfied at temperatures below 235 K. The ϵ_∞ values for eight samples measured parallel to the c-axis and six perpendicular to the c-axis are given in Figure 7. The values at temperatures above 240 K, which are taken from the literature (Johari, 1976), extrapolate to those below 253 K in a manner similar to that seen in polycrystalline ice (Gough, 1972). This indicates that our present measurements of ϵ_∞ perpendicular to the c-axis are consistent with the previous ones (Johari, 1976), although the equipment and the frequencies used in obtaining the ϵ_∞ values in the two measurements differ. It is evident in Figure 7 that the ϵ_∞ of ice parallel and perpendicular to the c-axis are the same within $\pm 0.5\%$.

The reason for a decrease in ϵ_∞ with temperature of polycrystalline ice has been a subject of discussion earlier (Gough, 1972; Johari, 1976; Johari and Jones, 1976[b]). In view of the observed isotropic behaviour of ϵ_∞ of ice, the discussion for single crystals of ice should be similar.

4.4. *The average relaxation time*

The average relaxation time τ_{av} was calculated from the frequency of maximum loss using the equation $\tau_{av} = (2\pi f_m)^{-1}$. The f_m values were obtained by plotting ϵ'' against the

logarithm of frequency on a large scale and interpolating. The τ_{av} for both the orientations of ice agreed, to within $\pm 5\%$, with Wörz and Cole's (1969) data and, at temperatures above 248 K, with Von Hippel and others' (1971), Ruepp's (1973), and Taubenberger's (1973) data.

According to Eyring's rate-process theory, the relaxation time for a molecular reorientation is given by,

$$\tau_{av} = (\tau_0/T)\, \exp\,(E^\star/RT),$$

where the pre-exponential factor τ_0 is given by,

$$\tau_0 = (h/ek)\, \exp\,(-S^\star/R),$$

h is Planck's constant, k is the Boltzmann factor, e is the transmission coefficient, $S^\star$ and $E^\star$ are the entropy and energy of activation respectively, and R is the gas constant. The product of τ_{av} and temperature is logarithmically plotted against the reciprocal temperature in
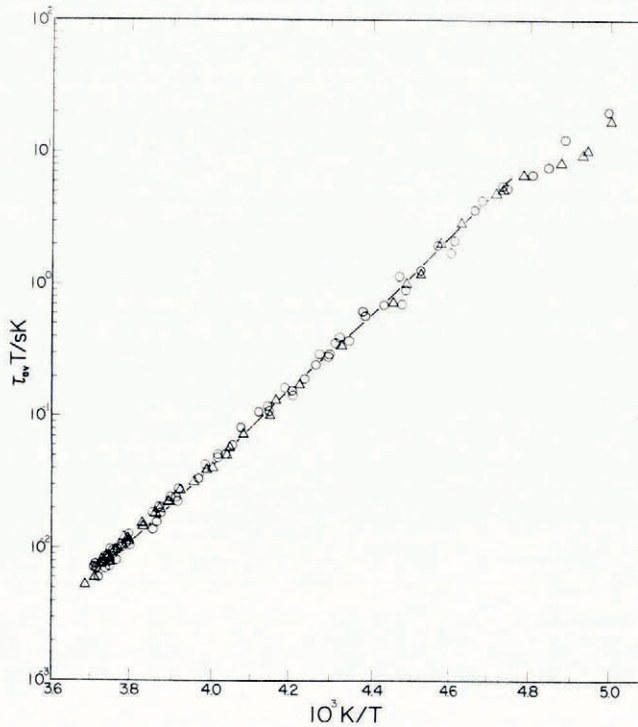

Fig. 8. *The variation of the product of the average relaxation time and temperature of ice plotted logarithmically against reciprocal temperature.* ◯, *parallel to the c-axis;* △, *perpendicular to the c-axis.*

Figure 8. The plot is linear in the temperature range 210–270 K. The values of τ_0 and $E^\star$ with standard deviation obtained from the least-square treatment of data for each of the two orientations and of the data for all samples and orientations are given in Table III.

The combined effect of the difference of τ_{av}, ϵ_0, and ϵ_∞ as a function of temperature between the various samples measured for the two orientations can be seen in Figure 9, where ϵ' and ϵ'' at 0.1 kHz are plotted against the temperature. At high temperatures the deviation from the average plot indicates the uncertainty in the measurement of $\Delta\epsilon$ for different samples and at low temperatures the uncertainty in τ values which contribute by a term $(1+\omega^2\tau^2)$ in ϵ' and $\omega\tau/(1+\omega^2\tau^2)$ in ϵ''. It is evident from Figures 8 and 9 that the relaxation time of ice is also isotropic between 210 and 271 K.
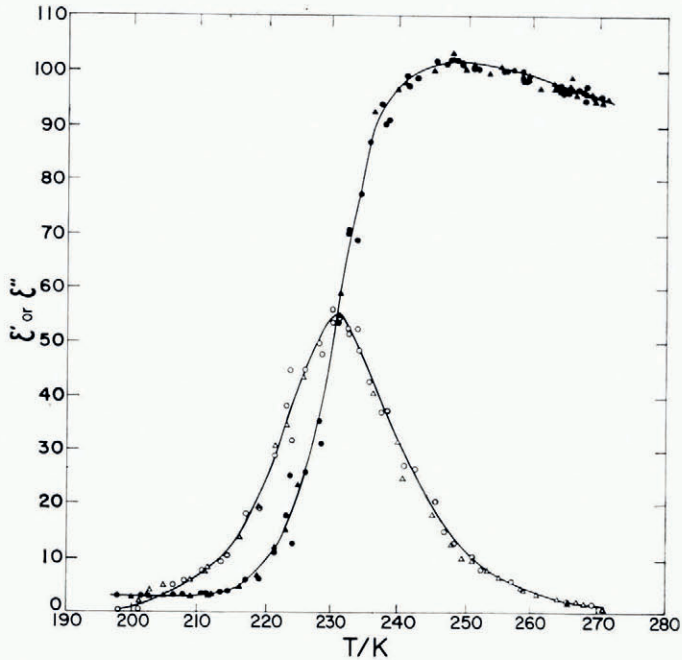
Fig. 9. The relative permittivity and loss of ice at 0.1 kHz plotted against temperature to show the combined effect of variation in τ_{av}, ϵ_0 and ϵ_∞ on the orientation of the sample. ○, parallel to the c-axis, and △, perpendicular to the c-axis. Open data points are for ϵ'' and filled data points for ϵ'.

The τ_{av} of ice for both the orientations follows the Eyring equation from 271 to 210 K with $E^\star = 51 \pm 2$ kJ mol⁻¹ and $S^\star = 18 \pm 2$ J mol⁻¹ K⁻¹, below which temperature the data show a large scatter and a trend towards a slope giving lower values of $E^\star$. The change towards a decreasing slope appears in Wörz and Cole's (1969) plot at c. 240 K, in Von Hippel and other's (1971) plot at c. 250 K and in Ruepp's (1973) plot at c. 230 K, although these workers have plotted τ_{av}, rather than $\tau_{av}T$, against T^{-1}. It is well recognized that the concentration of lattice defects has no effect on the steady-state polarization ultimately established, which is an equilibrium quantity: they provide only the mechanism by which it is established and their concentration determines the rate of establishment. A small amount of substitutionally or interstitially present impurity in zone-refined ice may produce orientational defects which at $T < 210$ K are more numerous than those produced by the thermal motion of water molecules in an ideal lattice and thus may cause $E^\star$ and $S^\star$ to become appreciably smaller. Gough and Davidson (1970) found that τ_{av} of polycrystalline ice, obtained from depressurizing ice II, was much higher than that of any sample of ice obtained by freezing water. The τ_{av}, however, decreased by several orders of magnitude when the ice was annealed. They proposed that the decrease in τ_{av} on annealing was caused by the dissolution of impurities, which had separated from hexagonal ice during its transformation to ice II and back into the hexagonal ice. It is noteworthy that impurities are thought to be much less soluble in the high-pressure phases of ice than in hexagonal ice, and indeed ice VI (Johari and Whalley, 1976) and ice VII (Johari and others, 1974) show no decrease in $E^\star$ with temperature. According to this interpretation, our zone-refined ice contains less impurity-produced orientational defects than any other sample of ice reported in the literature.

Gränicher (1969) and Bilgram and Gränicher (1974), after considering the τ_{av} and the d.c. conductivity together, have proposed that a decrease in $E^\star$ with temperature is caused by a

change in the relaxation mechanism from the one dominated by diffusion of orientational defects to the one dominated by diffusion of intrinsic ionic defects. In this view the decrease in $E^\star$ is intrinsic to the nature of ice, although no high-pressure phase of ice has shown this behaviour. Furthermore, the change in the relaxation mechanism occurs at a temperature when $\sigma_\pm/p = \sigma_{DL}/q$ (Bilgram and Gränicher, 1974), where $\sigma_\pm$ and σ_{DL} are the conductivity due to ionic and Bjerrum defects and p and q are the effective charge associated with the defects, respectively. At this temperature the ϵ_0 should reach a minimum value given by, $\epsilon_0 \approx \epsilon_\infty$ (Jaccard, 1965). This has not been observed for the zone-refined ice by us, or by other workers. It seems, therefore, more plausible that a decrease in $E^\star$ with temperature is caused by the impurity-generated orientational defects rather than the intrinsic ionic defects in ice.

4.5. *The effect of ageing*

As shown in Table I, the stock from which the ice samples were obtained was 1–8 years old, yet their ϵ' and ϵ'' decreased on annealing when contained in the dielectric cell. A number of samples of ice, of both the orientations, were stored at 253 ± 2 K for periods ranging from one to five weeks. Measurements made after this period showed a decrease by as much as 50% in ϵ'' at the frequency closest to the low-frequency intercept of the complex-plane plot, an increase of 0.5% in τ_{av}, but no change in $\Delta\epsilon$. One sample of ice oriented with the c-axis perpendicular to the electric field, contained in the Type KMT Capacitor, was kept at 253 ± 2 K for 11 weeks after the first measurement. Its $\Delta\epsilon$ and τ_{av} measured after this period showed a similar effect.

Taubenberger (1973) has reported that the $\Delta\epsilon$ of ice at 258 K measured perpendicular to the c-axis decreased by 1%, the ϵ_∞ increased by 10% and the τ decreased by 8%, when the ice contained between the electrodes was annealed at 258 K for 1 795 h. Another sample measured parallel to the c-axis at 248 K, showed no change in $\Delta\epsilon$ and τ but an increase in ϵ_∞ of 2%, when annealed for 110 h at that temperature. In our experience, the values of ϵ_∞ at 258 K extrapolated from measurements made only at kilohertz frequencies are somewhat uncertain, and little information is given by Taubenberger regarding the contribution to ϵ' and ϵ'' from space charge effects at low-frequencies. The change in τ in our measurement is apparently due to a reduction in the space charge polarization, as discussed in Section 4.1. Such changes are not likely to be intrinsic to ice.

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DISCUSSION

G. NOLL: Following the discussion about the anisotropy of ice Ih during the Symposium on Physics and Chemistry of Ice in Ottawa, 1972, Ruepp carried out dielectric measurements parallel and perpendicular to the electric field *with the same monocrystal*. He used a cylindrical sample with c-axis perpendicular to the cylinder axis. This elegant method avoids the difficulties and errors associated with the preparation of different samples. Rotation of the crystal in the field showed a clear anisotropy, but it was smaller than the value given by Humbel and others (1953).

R. TAUBENBERGER: Did you account for the error of $2\sigma_0\tau/\epsilon_0$ one commits in ϵ_0 by extrapolating a Cole–Cole semicircle for a Debye dispersion plus a constant σ_0? Could you give your $\sigma_0(T)$ values or at least values of $\omega\epsilon''$ minima you found in your Cole–Cole representations?

G. P. JOHARI: Yes, we did this by restricting the range by which ϵ' was to be extrapolated to obtain ϵ_0, although we doubt that the error in such analyses are entirely due to a non-zero value of σ_0, because there is a contribution from the space-charge polarization as well. The criterion we established for our analysis was that ϵ'' at the frequency nearest to the low-frequency end of the axis should be four or less, otherwise the extrapolated ϵ_0 would be in error by more than 0.5%. Some values of $\omega\epsilon''$ which you wish to know can be calculated from Figure 3 in the paper.

TAUBENBERGER: Did you not allow for an increasing width of relaxation times distribution with your ϵ_0 extrapolation method on going to lower temperatures so that your $\epsilon_0(T)$ is not directly comparable to what one gets on fitting for all temperatures to a simple Debye dispersion?

JOHARI: The ϵ_0 was obtained from an extrapolation of the complex-plane plots I had shown. In these plots ϵ' for the lowest frequency closest to the axis is not significantly different from the extrapolated ϵ_0. The increase in the half-width of the ϵ''–log f plots with decreasing temperature thus does not affect the accuracy of ϵ_0. Our $\epsilon_0(T)$ values are not strictly the same as ones obtained by assuming a simple Debye dispersion at temperatures where the ϵ''–log f plots are considerably broader than required by the Debye equation.

TAUBENBERGER: Could you comment on the relatively small activation energy for τ you obtained, corresponding to 0.527 eV in your whole temperature range, as compared to the usual 0.58 to 0.61 eV for higher temperatures lowering when $T < c$. 240 K depending on σ_0 behaviour?

JOHARI: The activation energy we obtained is 51 ± 2 kJ mol^{-1} or 0.53 ± 0.02 eV. This value is c. 0.02 eV lower than the Arrhenius energy corresponding to our plot, so, if you were to compare our value with the literature, you should use 0.55 ± 0.02 eV. I believe a comparison with the literature values would not be meaningful for two reasons: (1) we do not know the uncertainty in the literature values of Arrhenius energy and (2) the values in the literature were obtained, as you correctly indicate, from measurements made over a temperature range of c. 33 K but our value comes from a larger temperature range and even larger T^{-1} range.

TAUBENBERGER: Did you not see any change in capacitance due to flow of your samples which were under 3–4 bars uniaxial stress sometimes for several weeks at relatively high temperatures?

JOHARI: We observed no change in capacitance over a period of weeks when the sample was under a uniaxial stress of 3–4 bars.

TAUBENBERGER: As to Ruepp's data (1973); though this author does not decide definitely for anisotropy, his data on his figure 3 nevertheless strongly suggest also significant anisotropy as do the data of Von Hippel and others (1971), thus confirming at least qualitatively our own findings of an anisotropy $> 10\%$, confirming the early data of Humbel and others (1953).