

MEASUREMENTS OF THE ELECTRICAL PROPERTIES OF ICE Ih SINGLE CRYSTALS BY ADMITTANCE AND THERMALLY STIMULATED DEPolarIZATION TECHNIQUES

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ABSTRACT. Ice Ih single crystals were investigated by complex admittance and thermally stimulated depolarization (TSD) techniques, in the relaxation-time ranges 10^{-5} – 10 s and 10 – 10^4 s respectively.

The relaxation spectrum was resolved and three components of it were studied. Second-order kinetics had to be assumed for two of the TSD spectra to obtain Arrhenius-type relaxation times. The "Debye spectrum" had an activation energy for the relaxation time of 0.64 eV at the high temperatures and its dielectric strength revealed a possible defect cross-over at $T_c = 190$ K. Far below this temperature the activation energy was 0.38 eV, that is about half of that necessary for a pair of ion defects to form. In comparison with the results of other authors, a lower concentration of ionic defects, or possibly of Bjerrum-ion aggregates, was deduced to occur in our crystals.

Inert-gas host molecules were proposed as a possible origin of the two other spectra, having relaxation times shorter than the "Debye spectrum" and energies of 0.33 eV and 0.37 eV. Moreover the 0.33 eV spectrum, whose dielectric strength appears at a temperature below T_c , might alternatively be related to the cross-over of the "Debye spectrum".

RÉSUMÉ. Mesures des propriétés électriques de monocristaux de glace Ih par des techniques d'admittance et de dépolarisation thermique. Des monocristaux de glace ont été étudiés par des techniques diélectriques et par la méthode du courant de dépolarisation thermique (C.D.T.) correspondant respectivement à des temps de relaxation de 10^{-5} – 10 s et 10 – 10^4 s.

Le spectre de relaxation a été analysé et 3 de ses composantes ont été étudiées. Une cinétique du second ordre est envisagée par deux d'entre elles (spectre C.D.T.) conduisant ainsi à un temps de relaxation obéissant à la loi d'Arrhenius. Le spectre Debye correspond à un temps de relaxation avec une énergie d'activation de 0,64 eV à haute température; l'intensité de relaxation présente une anomalie vers $T_c = 190$ K. Bien au-dessous de cette température, l'énergie d'activation est de 0,38 eV, c'est à dire la moitié de l'énergie nécessaire à la formation d'un couple de défauts ioniques. Comparées aux résultats d'autres auteurs, ces données conduisent dans le cas de nos échantillons à une concentration en défauts ioniques (ou agrégats ion-défauts de Bjerrum) plus faible.

Une origine possible de deux autres composantes du spectre pourrait être associée à la présence de molécules de gaz mixte en insertion: les temps de relaxation sont alors plus courts que dans le cas de la relaxation de Debye et l'énergie d'activation est de 0,33 et 0,37 eV. En outre, la composante correspondant à l'énergie d'activation 0,33 eV et dont l'intensité de relaxation est notable en-dessous de T_c pourrait être reliée à l'anomalie de la relaxation Debye observée vers T_c .

ZUSAMMENFASSUNG. Messungen der elektrischen Eigenschaften von Eis-Ih-Einkristallen mittels Admittanz- und thermisch stimulierter Depolarisationsverfahren. Eis-Ih-Einkristalle wurden durch Admittanz- und thermisch stimulierte Depolarisations-(TSD-)Verfahren im Bereich der Relaxationszeiten 10^{-5} – 10 s bzw. 10 – 10^4 s untersucht.

Das Relaxationsspektrum wurde aufgelöst und drei Anteile davon wurden untersucht. Kinetik zweiter Ordnung musste für zwei der TSD-Spektren angenommen werden, um Relaxationszeiten vom Arrheniustyp zu erhalten. Das "Debye-Spektrum" hatte bei den hohen Temperaturen eine Aktivierungsenergie für die Relaxationszeit von 0,64 eV und sein dielektrischer Relaxationsbetrag zeigte eine mögliche Fehlerübernahme bei $T_c = 190$ K. Weit unterhalb dieser Temperatur betrug die Aktivierungsenergie 0,38 eV; dies ist ungefähr die Hälfte dessen was für die Bildung eines Ionenfehlerpaares nötig ist. Aus dem Vergleich mit den Ergebnissen anderer Verfasser wurde eine niedrigere Konzentration der Ionenfehler, oder möglicherweise Bjerrum-Ionen-Aggregate, für unsere Kristalle abgeleitet.

Inerte Gastmoleküle werden als mögliche Ursache der beiden anderen Spektren vorgeschlagen; sie haben kürzere Relaxationszeiten als das "Debye-Spektrum" und Energien von 0,33 eV und 0,37 eV. Das 0,33 eV-Spektrum, dessen Relaxationsbetrag bei einer Temperatur unterhalb T_c auftritt, könnte wahlweise zum Übergang des "Debye-Spektrums" in Beziehung gesetzt werden.

INTRODUCTION

The dielectric properties of ice, though extensively investigated in recent years, are still worth a thorough examination in order to be completely determined.

Apart from some discrepancies among the results of certain authors, further investigations are justified by the acknowledgement that even in undoped ice other mechanisms are present

(Von Hippel and others, 1972; Ruepp, 1973), beyond the already known Debye spectrum, and that other quantities such as for example the dielectric strength, must be investigated in more detail. Furthermore the temperature range in which the ice spectrum is known is not wide and its extension to lower temperatures is therefore desirable.

The experimental technique of thermally stimulated depolarization has been proposed by some authors (Bishop and Glen, 1969; Jeneveau and others, 1972; Johari and Jones, 1975) as a complement to dielectric constant measurements in the lower temperature range.

We wished to investigate the behaviour of samples of monocrystalline "pure" ice Ih by means of both these techniques to verify the coincidence of the results, and, if this is the case, to extend towards lower temperatures the range in which the dielectric relaxation of ice is known.

I. ADMITTANCE MEASUREMENTS

Experimental

For both admittance and depolarization measurements the electrodes were circular parallel plates, the upper electrode having a diameter of 18 mm with a guard-ring with inner diameter 20 mm and outer diameter 35 mm mounted on a teflon disk; the samples were monocrystalline disks (24 mm in diameter, 2 to 5 mm in thickness) with the *c*-axis normal or parallel to the electrodes, which were pressed against the sample surfaces by the long steel rods on which they were mounted, somewhat like sugar tongs.

The samples were cut from cylindrical monocrystals grown in the laboratory in lucite tubes, at the rate of $0.05 \mu\text{m s}^{-1}$. We used a modified Bridgman method, starting from out-gassed water with a conductivity of $10^{-5} \Omega^{-1} \text{m}^{-1}$ (at 25°C and 2 kHz).

To avoid accidental sample fractures caused by mechanical stresses induced by the electrodes during the thermal cycles, the interfaces with the ice were never frozen. Some measurements were also made with mica layers between the ice and the electrodes. The sample surfaces were flattened by lapping with alumina paper and silk cloth, after the removal of an ice layer of about 1 mm contiguous to the cut surfaces. A pressure of about 1 bar was applied to the electrodes to avoid air gaps at the interfaces.

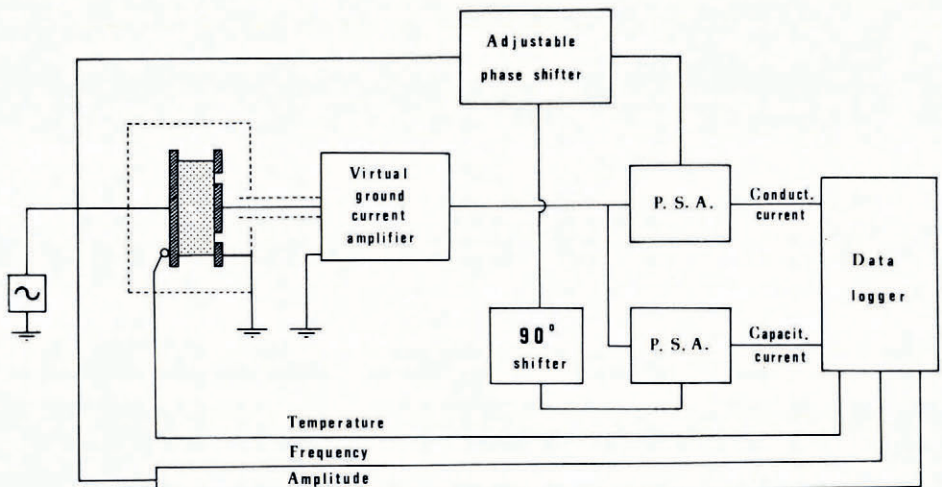


Fig. 1. Diagram (not to scale) of the apparatus used for the measurements of the complex admittance at frequencies higher than 0.1 Hz.

To measure the admittance at frequencies higher than 0.1 Hz, we made use of the phase-sensitive system sketched in Figure 1. For lower frequencies, in the range 2 to 10^{-3} Hz, a circuit quite similar to the other (Fig. 2) measured the integral of the current across the sample during a half-period, starting at the time the applied voltage reached zero or its peak value.

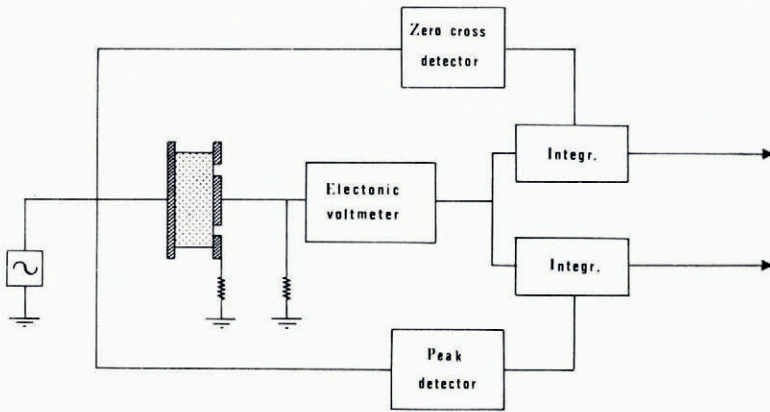


Fig. 2. Diagram (not to scale) of the apparatus used for the measurements at frequencies between 10^{-3} Hz and 2 Hz.

Results and observations

The relative dielectric constant k' and relative loss k'' were calculated from the experimental values of the equivalent parallel conductance and capacitance, whose absolute values were obtained by comparison with standard resistors and capacitors. As the plots of k' and k'' as functions of the frequency clearly show the composite nature of the spectrum, we analysed it with the sum of between one and three parallel mechanisms each with Debye relaxation, plus a d.c. conductivity:

$$k' = k_{\infty}' + \sum_i \frac{\Delta k_i}{1 + \omega^2 \tau_i^2}, \quad (1)$$

$$k'' = \sum_i \frac{\Delta k_i \omega \tau_i}{1 + \omega^2 \tau_i^2} + \frac{\sigma_{dc}}{\epsilon_0 \omega}, \quad (1')$$

where Δk_i is the dielectric strength of the i th dispersion, $\tau_i = \tau_0 \exp(E_i/k_B T)$ is its relaxation time, E_i its activation energy, ω the angular frequency, ϵ_0 the permittivity of free space, and k_{∞}' the high-frequency relative permittivity of ice, taken as 3.2. The data were fitted to these equations and the parameters obtained.

In Figure 3 we present the values of the relaxation times for one of our samples obtained from the admittance data, plotted against the reciprocal temperature. As stated above, at constant temperature the existence of superimposed relaxation mechanisms is suggested by the many steps in the curves of k' and k'' . When the temperature is changed, the continuity of the relaxation time and of the dielectric strength Δk_i convinces us that the same mechanism is being observed. In the case of the spectrum usually referred to as "Debye spectrum" (S_2 in Fig. 3) there are specific reasons for dropping the continuity requirement.

We observed four spectra, indicated as S_1 , S_2 , S_3 and S_4 in order of increasing relaxation frequency. We did not investigate in detail the spectrum S_1 but we simply ascertained its presence, always at the lowest frequencies of measurement. We attributed this spectrum to space charge at the electrodes.

Considering spectrum S_2 , we observe two distinct behaviours as a function of the temperature. In the range $T > T_c = 190$ K the plot of $\ln \tau_2$ has a slope equivalent to an activation energy of 0.64 eV, with a value of $\tau_0 = 7.7 \times 10^{-16}$ s. As may be expected a certain scatter in the results is found from sample to sample, a few of them showing a somewhat lower slope (down to 0.60 eV). The value of 0.64 eV coincides with that found by Camplin and Glen (1973) for the Debye spectrum, and is the highest among those reported in literature. Since the pre-exponential factor is also of the right order of magnitude, we identify the spectrum S_2 with that due to the reorientation of the water dipoles caused by intrinsic Bjerrum defects.

In Figure 3 it can be seen that at temperatures lower than T_c the slope of $\ln \tau_2$ decreases and then increases again, as in the spectrum reported by Ruepp (1973).

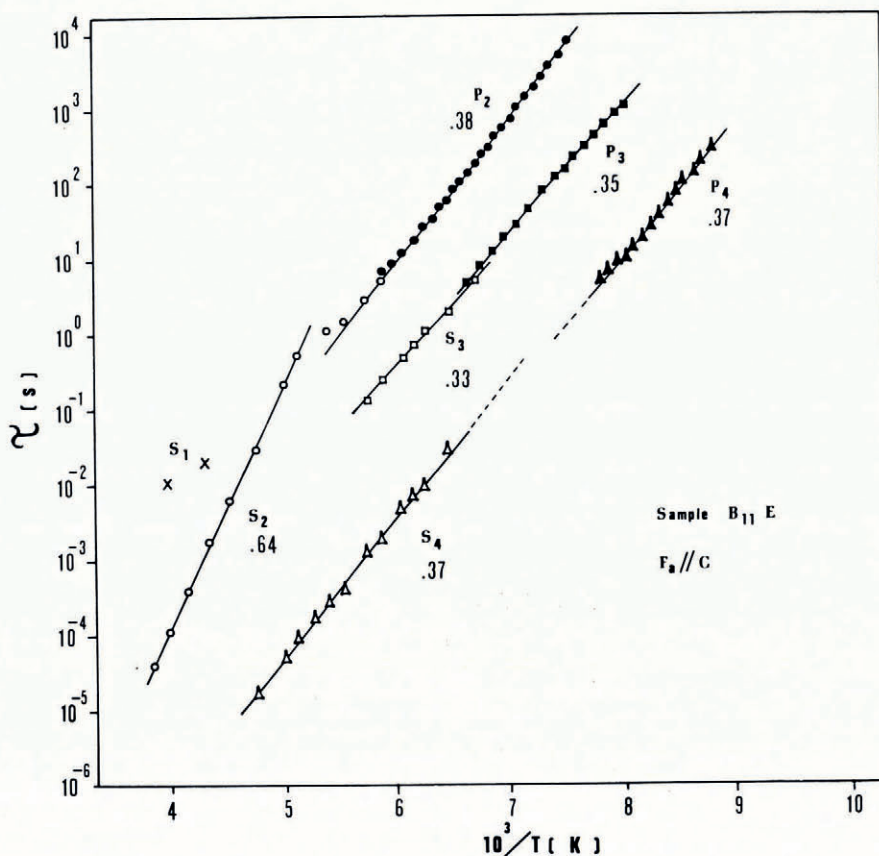


Fig. 3. Values of the relaxation times obtained from measurements of admittance (open symbols) and from TSD measurements (full symbols) as a function of the reciprocal temperature. The figures below the designations of the spectra indicate the energies in electron volts deduced from the best-fitting straight lines.

In Figure 4 the dielectric strength of the spectrum S_2 is plotted as a function of the reciprocal temperature. As can be seen, at a temperature of around T_c Δk has a pronounced decrease. The existence of a minimum in Δk and of a related change in the activation energy of τ is also found for crystals doped with HF (e.g. by Camplin and Glen, 1973). In the treatment given by Jaccard (1959, 1964) this behaviour is expected when the numerical current of Bjerrum defects equals that of ions. These latter defects are replaced by Bjerrum-ion aggregates in the model proposed by Bilgram and Gränicher (1974). An increase of the

minimum temperature for Δk with increasing HF concentration seems now established. A second minimum in Δk appears in samples with an HF concentration higher than 10^{-5} mol l $^{-1}$; this second minimum occurs at higher temperatures than the first one, and seems not to be associated with anomalies of τ . The lowest measured temperature of a Δk minimum in HF doped samples, as far as we know, is about 200 K, reported by Von Hippel and others (1972); the dopant concentration in their crystal was less than 10^{-8} mol l $^{-1}$. The curve of Δk_2 of Figure 4 is similar to a curve of HF-doped ice with a minimum of the first type. The temperature at which our minimum occurs is lower than that which would occur with the doping concentration of about 10^{-8} mol l $^{-1}$ reported above. The authors just mentioned also report that for crystals which are chemically pure but with some amount of crystalline imperfections, the Δk tends to decrease at low temperatures, together with a bending of the $\ln \tau$ graph. Unfortunately even for the samples that do not show the bending, the reported measurements stop at 190 K. Therefore in the common temperature range of measurement, our results are in substantial agreement with theirs.

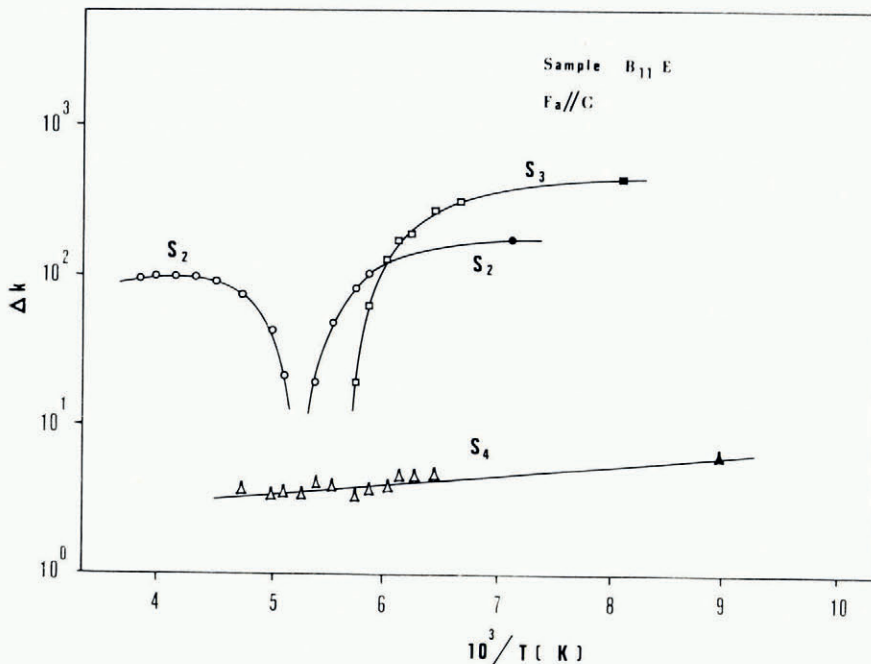


Fig. 4. Values of dielectric strength Δk obtained from measurements of admittance (open symbols) and from TSD measurements (full symbols) as a function of the reciprocal temperature. The same symbols as in Figure 3 have been used for each spectrum.

However as regards the results of Ruepp and Käss (1969), Ruepp (1973), Gough and Davidson (1970), and Camplin and Glen (1973), the agreement is restricted to the simple bending of the $\ln \tau$ graph. In the first two papers a change in the activation energy is reported for the intrinsic spectrum of "pure" ice between 230 K and 210 K, while only Ruepp reports that the dielectric strength tends to decrease, at much lower temperatures, about 120 K. Camplin and Glen, for "pure" ice in the range 270–220 K, and Gough and Davidson, for reconverted ice (I \rightarrow II \rightarrow I), measured activation energies similar to that we found for τ_2 at the higher temperatures, but did not find any decrease in Δk down to the lowest temperatures of measurement.

At temperatures a little lower than that at which $\ln \tau_2$ changes its slope a new spectrum S_3 appears, whose dielectric strength, reported in Figure 4, increases rapidly. This spectrum also has a Debye behaviour, with an activation energy of 0.33 eV and a value of τ_0 of 4.0×10^{-11} s.

A further spectrum S_4 , with a dielectric strength almost constant with the temperature (Fig. 4) is observed at the higher frequencies of measurement, down to a temperature of 155 K, after which it was no more observable. Apart from the larger values of the activation energy we found, 0.37 eV, it behaves like that referred to as the high-frequency spectrum by Ruepp (1973). The appropriate value of τ_0 for S_4 is 2.5×10^{-14} s.

II. TSD MEASUREMENTS

Experimental

We investigated the behaviour of the ice samples in the low-temperature range, where the extrapolated values of the previously reported relaxation times are of the order of tens of seconds, by thermally stimulated depolarization current measurements, without changing the experimental set-up.

The TSD measurements were made by cooling the ice samples under an applied static electric field and by subsequently heating them, after the field had been removed. The constant heating rate $dT/dt = \alpha$ was of the order of 0.1 K s^{-1} , and the current was measured as potential difference across a calibrated resistance of 10^8 to $10^{10} \Omega$, by means of an electrometer with $10^{15} \Omega$ input impedance and 10^{-3} s rise time.

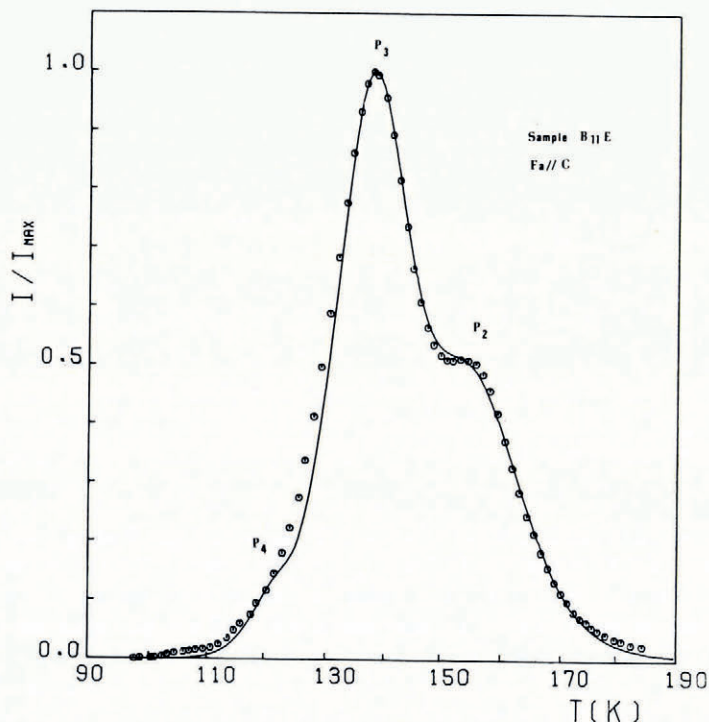


Fig. 5. TSD spectrum obtained by polarizing the sample between 190 K and 77 K, heating rate 0.11 K s^{-1} , polarizing field $F_a = 3 \times 10^4 \text{ V m}^{-1}$. (O) experimental points, (—) best fitting curves obtained as described in the text.

Results and observations

The TSD spectrum of "pure" ice crystals has been found to be quite complex from the experiments of Bishop and Glen (1969), Jenevau and others (1972), and Johari and Jones (1975); that of the same sample to which Figure 3 refers is shown in Figure 5. It was obtained by applying a polarizing field $F_a = 30 \text{ kV m}^{-1}$ from 190 K to 77 K; by so doing it was possible to suppress the whole high-temperature portion of the spectrum, which clearly appears to derive from a charge storage in front of the electrodes. As it is sufficient to apply the field at temperatures lower than 190 K to avoid this effect, we may think we are dealing with mobile charges probably trapped at the low temperatures in sufficiently deep traps, in agreement with the results of Gelin and Stubbs (1965).

The result shown in Figure 5 depends neither on the time during which F_a is applied nor on the use of partially blocking (i.e. gold or steel) or totally blocking (with two mica layers) electrodes. Two current peaks, P_2 and P_3 , can be clearly seen, while a third smaller peak is almost hidden in the first part of the curve; this peak can be shown up with respect to the other two, by applying a field of higher intensity than the previous one, in a short temperature range just below the temperature at which its current maximum is expected to occur. In general by the use of this procedure and also by partial discharges of the polarization, one can isolate the contiguous peaks of a TSD spectrum, provided their maximum temperatures are sufficiently distant. We succeeded in doing so for peaks P_2 and P_3 but not in the case of P_4 , because of the much higher efficiency of mechanism 3 with respect to 4. Therefore we think that these three peaks are mutually independent, that is their mechanisms can be activated separately.

In the analysis of a complete spectrum or of a peak isolated in the way described above, we made the following assumptions:

- (a) the TSD spectrum is given by the sum of the currents \mathcal{J}_t produced by distinct and independent mechanisms;
- (b) each mechanism in isothermal conditions is governed by a relaxation equation of the form

$$\mathcal{J} = -\frac{dP}{dt} = \frac{P}{\tau}, \quad (2)$$

where P is the polarization and τ the relaxation time;

- (c) for each mechanism τ has a temperature dependence of the form:

$$\tau = \tau_0 \exp \frac{E}{k_B T}, \quad (3)$$

with τ_0 and E constant.

Following Kauzmann (1942), τ_0 should be proportional to T^{-1} , but for our purposes this further temperature dependence can, to a first approximation, be neglected with respect to the exponential one.

Equation (2) with the use of Equation (3) and $dT/dt = \alpha$ can be integrated to give the current density \mathcal{J} for the relaxation kinetics:

$$\mathcal{J} = \frac{P(0)}{\tau_0} \exp \left[\frac{-E}{k_B T} - \frac{1}{\alpha \tau_0} \int_{T_0}^T \exp \left(\frac{-E}{k_B T'} \right) dT' \right], \quad (4)$$

where $P(0)$ is the polarization at the temperature T_0 at which the heating started.

According to Equation (2) the ratio P/\mathcal{J} gives the relaxation time of the mechanism at each temperature, whatever its temperature dependence, and if hypothesis (c) also holds, a plot of $\ln (P/\mathcal{J})$ versus $1/T$ would be a straight line. The value of P being found by integrating

the values of \mathcal{J} since $P(T) = \int_T^\infty \mathcal{J}(T') dT'$, these plots were drawn for each of the isolated peaks. We excluded all points with \mathcal{J} values lower than 10% of the maximum, but we found that only that plot which referred to P_4 was straight in a sufficiently wide temperature range; on the contrary the two plots referring to P_2 and P_3 showed humps. Furthermore in the plot of P_4 the points at the highest temperatures bent upwards. This bending was due to the P_3 peak contributing to the \mathcal{J} values at the higher temperature, it being impossible to suppress the contribution completely. Therefore to be able to determine the value of the activation energy by a different method, we used that proposed by Land (1969), which makes use of the condition to nullify the second derivative of the current with respect to the temperature, in either of the two curvatures.

The straight line corresponding to the values of E and of τ_0 obtained by this method (0.37 eV and 1.7×10^{-14} s) fits quite well the points of the low-temperature portion of the plot of $\ln(P/\mathcal{J})$ as shown in Figure 3; the values are in good agreement with those calculated at the higher temperatures for spectrum S_4 .

The irregular shape of the plots of $\ln(P/\mathcal{J})$ for peaks 3 and 4 may be due to one or both of the following reasons:

- (1) Equation (2) is not the correct one to describe the relaxation;
- (2) the observed peak is the result of a continuous distribution of relaxation times or the result of a number of inseparable mechanisms.

We succeeded in maintaining hypothesis (c) by dropping hypothesis (b) and assuming that the isothermal relaxation is described by second order kinetics; that is:

$$\mathcal{J} = -\frac{dP}{dt} = \frac{P^2}{P^*\tau}, \quad (5)$$

where P^* is a constant with the same dimensions as the polarization. With this hypothesis P^2/\mathcal{J} gives the product $P^*\tau$ and the logarithm of this quantity was actually linear as a function of $1/T$ for the peaks 2 and 3. Also in this case from the slopes of the two best-fitting straight lines we were able to obtain the values of the activation energies of mechanisms 2 and 3, which were 0.38 eV and 0.35 eV respectively; these values are very similar to those obtained for the dielectric spectra S_2 and S_3 at higher temperatures, but the τ_0 values are still unknown.

Assuming P^* to be equal to $P(0)$ (the polarization of the sample at time zero) we found that the pre-exponential factors τ_0 for both P_2 and P_3 (2.8×10^{-11} s and 1.4×10^{-11} s respectively) were of the right order of magnitude to give relaxation times comparable with those extrapolated from the higher temperatures values. The calculated τ are plotted in Figure 3 together with the best-fitting straight lines. These results were confirmed by means of Land's method, which in this case refers to the equation:

$$\mathcal{J}' = \frac{P(0)^2 \exp\left(-\frac{E}{k_B T}\right)}{\alpha P^* \tau_0 \left[1 + \frac{P(0)}{\alpha P^* \tau_0} \int_{T_0}^T \exp\left(-\frac{E}{k_B T'}\right) dT'\right]^2}. \quad (6)$$

The total current density $\mathcal{J}_{\text{tot}} = \mathcal{J}_2 + \mathcal{J}_3 + \mathcal{J}_4$, calculated with the values of E and of τ_0 reported above, fits the experimental data quite well, as shown by the solid line in Figure 5.

If we wish to investigate also the correlation between total initial polarization (stored charge) and applied field, we cannot have recourse to the experimentally isolated peaks, as the techniques for obtaining them reduce the value of $P(0)$ caused by the applied field. Therefore

we determined its true value from the fit of the complete spectrum. Each value so obtained can be thought of as a contribution to the sample polarization that freezes-in when the temperature is lowered while an electric field is being applied. We estimate that this happens when the relaxation time of the mechanism is larger than 10^3 s. Therefore the values of $P(o)_i$ obtained from the fit of the complete spectrum, are associated with the temperatures at which the respective τ have such a value.

The contributions Δk_i to the dielectric strength were calculated by using the expression:

$$\Delta k_i = 1 + \frac{P(o)_i}{\epsilon_0 F_a}, \quad (7)$$

and are plotted in Figure 4.

III. DISCUSSION

The main purpose of our investigation was the measurement of the single relaxation times of the spectrum of "pure" ice in the widest possible temperature range.

By the use of the same criterion of continuity used in plotting the dielectric spectra, we can conclude formally that the TSD relaxation times refer to the same spectra as are observed by the admittance measurements. To achieve this result we had to use a second-order differential equation to describe the depolarization of mechanisms 3 and 4.

Equation (5), which is formally similar to that describing the recombination kinetics of objects of opposite nature with equal non-equilibrium concentrations, implies a depolarization kinetics different from that valid for a uniform distribution of dipoles given by Equation (2). Therefore one should admit that the probability of each dipole changing its reorientation in unit time, $1/\tau$, is proportional to the polarization.

In ice, where the reorientation is thought to occur by the migration of defects, we should admit that their velocity or their out-of-equilibrium concentration is proportional to the sample polarization; these same ideas were also suggested by Bishop and Glen (1969). It is not easy to specify them in more detail in microscopic terms, but we think that the movement of space charge might be the dominant part of mechanisms 2 and 3.

Considering more closely the Debye spectrum of ice, S_2 , we must note first of all, that the slope we found indicates an activation energy for the formation of a pair of L and D defects of 0.80 eV, which is higher than the value usually reported, but is in agreement with the theoretical calculations (Hobbs, 1974, p. 131-40).

If in the ice crystal only the "classic" traffic of Bjerrum and ionic defects (or of Bjerrum-ionic aggregates) occurs, and if only these latter can sustain a d.c. conductivity σ_{sD} , then:

$$\sigma_{\infty D} - \sigma_{sD} = \frac{\epsilon_0 \Delta k_D}{\tau_D}, \quad (8)$$

when $\omega \gg 1/\tau_D$ at each temperature.

The current interpretation of the dielectric relaxation in ice is that at higher temperatures $\sigma_{\infty D}$ is determined by the majority Bjerrum defects, while σ_{sD} is determined by the minority ionic defects. On lowering the temperature a cross-over condition can be reached, where the numerical currents of the two kinds of defects are equal. Then

$$\sigma_{\infty D} = \sigma_{sD}, \quad \Delta k_D = 0, \quad (9)$$

at each ω .

At temperatures lower than that of the cross-over, an exchange in the roles occurs, with $\sigma_{\infty D}$ determined by ions and σ_{sD} by the Bjerrum defects.

In measurements like ours, in which more than one mechanism is present, we have:

$$\sigma_{\infty 2} = \sigma_{de} + \frac{\epsilon_0 \Delta k_1}{\tau_1} + \frac{\epsilon_0 \Delta k_2}{\tau_2}, \quad (10)$$

for ω such that $\omega\tau_2 \gg 1$, and therefore also $\omega\tau_1 \gg 1$.

We could also obtain from our measurements $\sigma_{\infty 2}$ and σ_{de} separately, but we cannot identify σ_{de} with σ_{0D} , the minority carrier conductivity in the Jaccard model, because from the TSD measurements we also identified, at temperatures higher than 190 K, extrinsic mobile charges.

However we can observe that, far from the cross-over, where $\sigma_{\infty D} \gg \sigma_{sD}$ in Equation (8), τ_2 and $\sigma_{\infty 2}$ have the same activation energy. The values we found for τ_2 above and below $T_c = 190$ K, are 0.64 eV and 0.38 eV, corresponding to 14.7 kcal/mol and 8.7 kcal/mol respectively, and are in good agreement with those obtained by Kahane (1969) for σ_{sD} (9 kcal/mol and 14 kcal/mol) by the use of ion-exchange membranes. Also the temperature at which the temperature dependence of σ_{sD} changes, in Figure 3 of his paper, is very similar to our T_c .

Therefore we can reasonably think that we are dealing with a defect cross-over at 190 K.

The efficiency of the ions is suggested by the energy found, 0.38 eV, comparable to that reported for their formation (Bullemer and others, 1969; Engelhardt and others, 1969).

We also found it interesting to compare our results with the model proposed by Bilgram and Gränicher (1974) proposing the presence of Bjerrum-ion aggregates. To do this we calculated $\sigma_{\infty D}$ by Equation (8) from our values of τ_2 and Δk_2 measured at high temperatures, and obtained the extrapolated value of $\sigma_{\infty 2}$ at T_c .

This value was of the order of $10^{-9} \Omega^{-1} m^{-1}$ in good agreement with that at 190 K deduced from the plot of the cross-over conductivity σ_c reported by those authors.

The meaning of so low a cross-over temperature can be found in the observation that σ_{sD} must also be lower in our case. Since we do not find any variation of the high-temperature portion of spectrum S_2 , determined by Bjerrum defects, we must suppose that the concentration of ions available to form aggregates is, in our crystals, appreciably lower than those giving the results reported by Bilgram and Gränicher and referred to in their Figure 1.

Spectrum S_4 is typical of a relaxation of dipoles uniformly distributed in the sample. Because of its dielectric strength and of the high relaxation frequency, it is reasonable to attribute it to water molecules loosely bonded to the lattice. Ruepp (1973) proposed that their origin could be found in the microstructures described by Truby (1955).

Although this is certainly possible, we are also attracted by the possibility suggested by Johari and Jones (1976), that inert gas molecules, like those that can form clathrate hydrates, could locally modify the reorientation rate of water dipoles and the corresponding activation energy.

As regards spectrum S_3 , although it only arises below 170 K and its Δk rapidly attains high values, and could therefore be related to the cross-over, we observe that because of its values of activation energy and relaxation times, it could have an explanation similar to the second one advanced for spectrum 4.

Gough and others (1968), in fact obtained for water molecules in nitrogen clathrate a dielectric relaxation with $E = 7.9$ kcal/mol and τ ($^{\circ}C$) = 1.5×10^{-5} s, where we find for spectrum S_3 $E = 7.6$ kcal/mol and τ ($^{\circ}C$) = 4.9×10^{-5} s.

IV. CONCLUSIONS

The apparent purity of some of our samples (if not a compensation) has enabled us to ascertain that in certain conditions Bjerrum defects may remain the majority carriers in governing the dielectric relaxation in ice, at least down to 190 K, and that at lower temperatures this role is played either by ions or by Bjerrum-ion aggregates.

The TSD technique seems to give results similar to those obtained by dielectric relaxation measurements, provided that, in certain cases, one assumes a depolarization kinetics different from that shown to be valid at the higher temperatures, in frequency-dependent measurements.

Further experimental investigations and furthermore a careful analysis of the thermally stimulated depolarization kinetics in real ice crystals will be necessary to clarify this discrepancy.

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DISCUSSION

M. ELDRUP: Could you possibly associate one of your relaxation times with the migration of vacancies?

U. DEL PENNINO: In Mogensen and Eldrup (1978) you report values of the vacancy concentration and of their energies of formation and migration that could be compatible with the results that refer to the high-temperature portion of spectrum 2, but the idea of substituting vacancies for Bjerrum defects as the origin of this spectrum would involve a general revision of the theory. As regards spectra S_3 and S_4 , with relaxation times lower than S_2 and that can be independently activated, their contributions to the dielectric strength seem to be too high to be associated with the reorientation of molecules adjacent to vacancies or vacancy clusters.

R. TAUBENBERGER: Have you also measured the $\sigma_0(1/T)$ of the so-called Debye dispersion, in other words measured the entire complex $\epsilon^*(\omega)$?

DEL PENNINO: As already said in the full paper, we have not yet investigated in detail the temperature dependence of σ_0 .

G. P. JOHARI: Have you looked at the complex-plane plots of the real and imaginary part of the complex permittivity?

DEL PENNINO: Yes, in some cases we also considered the plot of k'' versus k' . It could be described as a "sum" of semicircular curves.

JOHARI: I would like to point out that there is a serious problem in thermally stimulated depolarization measurement, namely, one of identifying the orientation polarization peak from space-charge polarization peaks. The only method of distinguishing between them that I know of is to measure the total charge associated with the peak as a function of the magnitude of the electric field applied and also as a function of either the thickness and/or the area of the ice sample. If the total charge under a peak increases linearly with the field and also linearly with the geometric capacitance of the cell, the peak is due to orientation polarization. If not, it is due to space-charge polarization. I wonder if your data satisfy the criteria for the identification of the peak as due to the orientation polarization?

DEL PENNINO: I agree with you on the criteria; furthermore in a case like this in which the temperature during the polarization changes linearly with the time, the maximum temperature of a peak T_m should be independent of the way in which the sample is polarized if the peak is due to orientational polarization. In the case of space-charge, T_m should depend on the procedure used to polarize the sample, because in this case the initial charge distribution changes accordingly. During the procedures to isolate the peaks experimentally we observed that T_m is independent of them. As regards the relationship between field intensity and the charge associated with the peak, we refer, for the reasons stated above, to the values of $P(o)_i$ used to fit the complete TSD spectrum. For the same sample these values change linearly with the field up to 30 kV/m, but we intend to verify this behaviour at higher field intensities to have conclusive results. To change the width of the sample we had to use, of course, three samples of different thickness. In this case we have some scatter in the results, but they are still compatible with a linear relationship between charge and width.

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