Depolarization Thermocurrents in Ice Ih at Low Temperature

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Z. Naturforsch. **36a**, 321–328 (1981); received December 10, 1980

Polycrystalline ice samples frozen from highly purified water have been investigated by means of the depolarization thermo-current (DTC) technique in the temperature range 85–250 K. Three peaks have been observed at temperatures about 125, 165, and 225 K at a heating rate of 3.5 K/min. The measurements confirm most of the results reported by Johari and Jones. The characteristics of the low temperature DTC peak have been examined extensively for different samples, different heating rates and different polarization conditions. This peak has been found to be non-Debye. Its multiplicity has been studied experimentally using the possibilities offered by the DTC method. It may be better represented by a continuous ditribution of relaxation times than by a sum of discrete relaxation processes.

Introduction

The dielectric properties of pure ice crystals are of great interest and have been widely studied. A true molecular understanding of them is, for example, presupposed in the study of the state of water in hydrated biological materials by dielectric methods.

Ordinary ice forms a hexagonal lattice (ice Ih) [1]. The O-atoms are in an arrangement of approximately tetrahedral symmetry. They are linked by hydrogen bonds governed by the following Bernal-Fowler rules: 1) There is one and only one H-atom between two O-atoms. 2) Two H-atoms are close to one O-atom. There are six possible orientations for every H_2O molecule and hence a vast number of possible hydrogen arrangements in an ice crystal, which are compatible with the Bernal-Fowler rules. According to Pauling's hypothesis [2] and in consistency with experimental results all these arrangements are equally likely to occur (orientational disorder).

If one assumes that the Bernal-Fowler rules are strictly valid, one has no explanation for the dielectric relaxation and for the DC-conductivity in ice. One has to admit that they are locally violated. For the dielectric properties of ice two types of intrinsic defects are of importance [3]:

1) ionic defects (H_3O^+ and OH^-). They are produced in pairs by shifting of the protons along the O–O bonds.
2) Bjerrum defects (also orientational defects). A proton can make a rotational motion to a neighbouring bond. Thus a doubly occupied bond (D-defect) and a vacant bond (L-defect) are generated.

In addition to these intrinsic defects in the ideal lattice, extrinsic physical and chemical defects such as vacancies, dislocations, grain boundaries, interfaces, and impurities are also present in every ice sample.

Using bridge techniques many investigators [4–9] have observed a dielectric relaxation with a single relaxation time τ obeying the Arrhenius equation

$$\tau = \tau_0 \exp(W/kT) \qquad (1)$$

(Debye behaviour) at high temperatures. In this equation W is the activation energy for the dipole reorientation, k is Boltzmann's constant, T is the absolute temperature and τ_0 is the so-called pre-exponential factor. W was found to be about 0,60 eV and τ_0 in the range of 10^{-16} sec. At low temperatures deviations from Debye behaviour, a change to shorter relaxation times and a lower activation energy (typically 0.26 eV) have been observed. The bending over has been found to occur at temperatures between 243 and 203 K depending on the sample. The common explanation for this is that the Debye behaviour at high temperatures is related

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with intrinsic Bjerrum defects, while the deviations at low temperatures are due to extrinsic defects, probably generated by impurities. On the other hand, on the basis of Jaccard's theory [10], Gränicher [11] suggested that there is a real change in the relaxation mechanism at temperatures between 233 and 203 K depending on the sample from one determined by intrinsic Bjerrum defects at high temperatures to one in which intrinsic ionic defects play the dominant role.

By means of the depolarization thermocurrents (DTC) technique Engelhardt and Riehl [12] have observed in single ice crystals a current peak at 119 K at a heating rate of 1.0 K/min. The activation energy has been found to be about 0.2 eV. This peak has been attributed to space charge limited proton currents. Using the same technique and single crystals Jeneveau et al. [13, 14] have observed three current peaks at 119, 160 and 179 K at a heating rate of 3.0 K/min. The low temperature peak with $W = 0.21$ eV and $\tau_0 = 5.4 \times 10^{-8}$ sec has been related with conductivity in ice. The 160 K-peak with $W = 0.28$ eV and $\tau_0 = 1.1 \times 10^{-7}$ sec has been ascribed to ionic states, while the 179 K-peak with $W = 0.60$ eV and $\tau_0 = 6.2 \times 10^{-16}$ sec has been ascribed to Bjerrum defects. Using the DTC method and polycrystalline samples Johari and Jones [15] have observed three current peaks at 110.4, 159 and 233 K at a heating rate of 0.14 K/min. The low temperature peak has been attributed to the relaxation of frozen-in orientation polarization of water molecules in ice. The characteristics of this peak

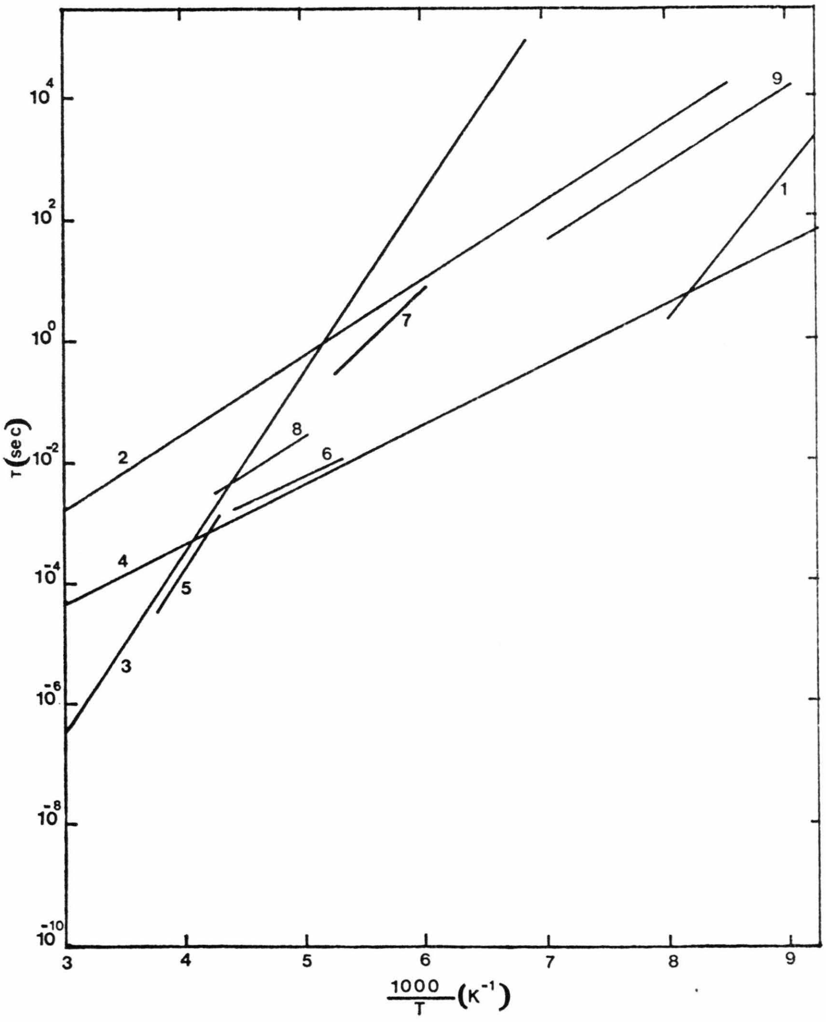

Fig. 1. The dielectric relaxation time of ice measured in dielectric loss experiments and calculated from DTC measurements plotted against reciprocal temperature. **1**: Ref. [15] (DTC, step-responce, bridge); **2**: Ref. [13, 14] (DTC, $\tau_0 = 1.1 \times 10^{-7}$ s, $W = 0.28$ eV); **3**: Ref. [13, 14] (DTC, $\tau_0 = 6.2 \times 10^{-16}$ sec, $W = 0.60$ eV); **4**: Ref. [14] (DTC, $\tau_0 = 5.4 \times 10^{-8}$ sec, $W = 0.21$ eV); **5**: Ref. [4, 5, 7] (bridge); **6**: Ref. [7] (bridge); **7**: Ref. [7] (bridge); **8**: Ref. [6] (bridge); **9**: this work.

$W = 0.50$ eV and $\tau_0 = 5 \times 10^{-20}$ sec · K have been obtained according to Eyring's rate process theory as extended by Kauzmann [16]. The peak has been found to be multiple.

In Fig. 1 values of the relaxation time τ measured in dielectric loss experiments and values calculated from DTC measurements are plotted logarithmically against reciprocal temperature.

It is evident from this short review that further study of the dielectric properties of ice is needed. This paper presents a detailed study of the low temperature DTC peak in ice Ih. Our interest is mainly in studying the multiplicity of the peak, the variation of its characteristics for different samples heated at the same rate and the variation of the maximum temperature T_{M} for different heating rates for the same sample.

Experimental

The principle of the DTC method is very simple [17]: The sample is polarized by an applied electric field E_{p}. This polarization is subsequently frozen in by cooling the sample down to a temperature T_0 sufficiently low to prevent depolarization by thermal energy. The field is then switched off and the sample is warmed up at a constant rate b while the depolarization current as the dipoles relax is detected by an electrometer.

In the case of a single relaxation obeying the Arrhenius equation (1), the depolarization current density $J(T)$ is given by the equation

$$J(T) = (P_0/\tau_0)\exp(-W/kT) \cdot \exp\left[-\frac{1}{b\,\tau_0}\int_{T_0}^{T}\exp(-W/kT')\,\mathrm{d}T'\right], \tag{2}$$

where P_0 is the initial polarization. W is obtained by plotting $\ln J$ against $1/T$ or, more precisely, by plotting $\ln[P(T)/J(T)]$ against $1/T$. τ_0 is then obtained from the equation

$$\tau_0 = (k T_{\mathrm{M}}^2/bW)\exp(-W/kT_{\mathrm{M}}), \tag{3}$$

where T_{M} is the temperature of the peak maximum.

We used a common experimental apparatus. The polycrystalline ice samples (cylinders of approximately 4 mm diameter and 1 mm height) were grown in the measuring capacitor made of brass. This guaranteed good electrode contact. The water used was double-distilled and deionized. Its DC conductivity was 6×10^{-7} Ohm^{-1} · cm^{-1}.

Two series of experiments were carried out:

a) After the sample was cooled under the influence of an electric field (1.0–6.0 kV/cm) from 250 K to less than 90 K at a rate of about 4 to 6 K/min, the field was removed and the sample heated to 250 K at a constant rate to insure that all possible peaks between 90 K and 250 K would be observed.

b) In order to further determine more accurately the characteristics of the low temperature DTC peak, the field was applied to the sample at a temperature T_{p} (usually near the temperature of the peak maximum) for a time t_{p} (usually 5 min). The temperature was then lowered rapidly to less than 90 K, at which point the applied voltage was removed and the sample heated at a constant rate.

Results

In Fig. 2 the DTC is plotted against temperature in the range 90–250 K for a sample on heating at a rate of 3.5 K/min. The sample was polarized by cooling from 250 to less than 90 K under the influence of a field of 3 kV/cm. The plot shows two predominant peaks at 125 and about 225 K and a smaller one at about 162 K.

Figure 3 shows the low temperature DTC peak (at 126 K) for another ice sample polarized for 10 min at 130 K with 3 kV/cm and heated at a rate of 3.5 K/min. The dashed curve was calculated from (2) using the measured values for W and τ_0, and then normalized. For the integral in (2) the approximation suggested by Squire [18] was used. This approximation is

$$F(T,W) = T\exp(-X)\,\frac{X + C_1}{X^2 + C_2 X + C_3},$$

where

$$F(T,W) = \int_{T_0}^{T}\exp(-W/kT')\,\mathrm{d}T', \tag{4}$$

$$X = W|kT,$$

and

$$C_1 = 3.0396, \quad C_2 = 5.0364, \quad \text{and} \quad C_3 = 4.1916.$$

We studied twenty samples. The peak temperature T_{M} was found to vary for different samples for the same heating rate by as much as 6 K. On the other hand, T_{M} was never found to vary by more than 2 K for different runs made with the same sample

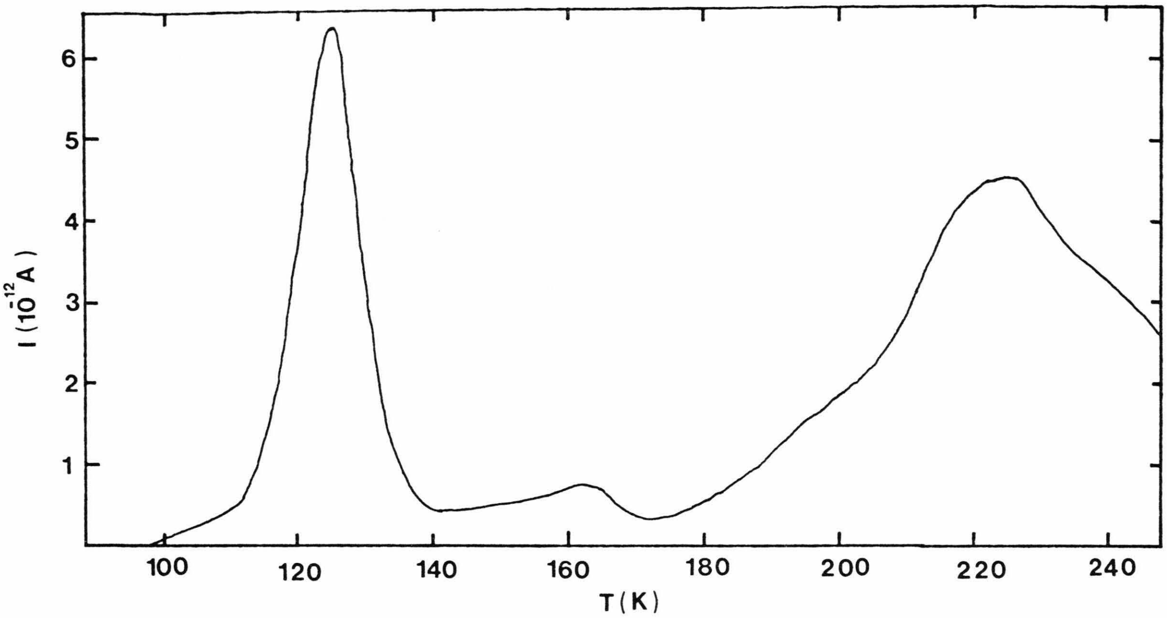

Fig. 2. The DTC plot for an ice sample polarized by cooling from 250 to less than 90 K under the influence of an electric field of 3.0 kV/cm. The heating rate was 3.5 K/min.

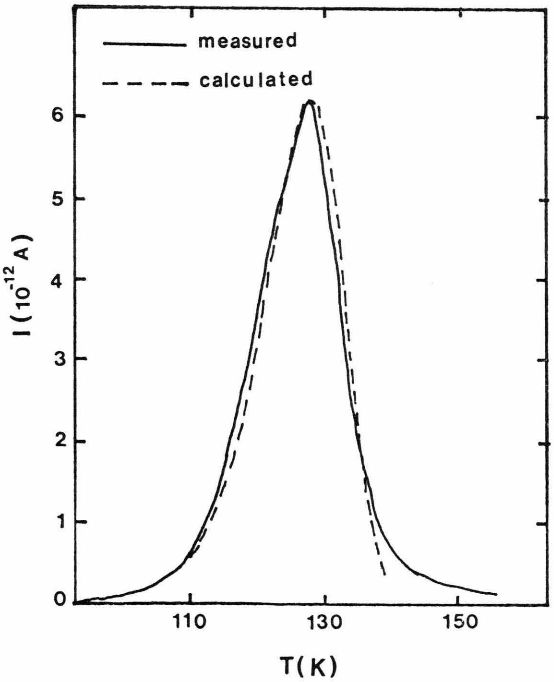

Fig. 3. Comparison of the measured and the calculated low temperature DTC peak for an ice sample polarized for 10 min at 130 K with 3 kV/cm and heated at a rate of 3.5 K/min.

at the same heating rate. The mean value for T_M was found to be 125 K. The activation energy for the dipole reorientation W was obtained from plots of $\ln I$ versus $1/T$ (initial rise method). In general W could not be determined from plots of $\ln P/I$ versus $1/T$ (whole curve method): it was impossible to draw a straight line through the experimental points. W was found to vary for different runs made with the same sample and for different samples by as much as 0.02 and 0.03 eV respectively. The corresponding variation in τ_0 was very large, so that only the order of magnitude of τ_0 could be determined. This is due to the exponential dependence of τ_0 on W and T_M, Equation (3). The mean value for W was found to be 0.25 eV. The range of τ_0 was 10^{-9} sec.

The activation energy W can also be obtained but with less precision from the variation of the peak temperature T_M for different heating rates for the same sample. From (3) it follows that

$$\frac{T_M^2}{b} = \frac{W\tau(T_M)}{k} = \frac{W}{k}\tau_0 \exp\left(\frac{W}{k T_M}\right), \quad (5)$$

always under the assumption of exponential variation of the dipolar relaxation time τ with tempera-

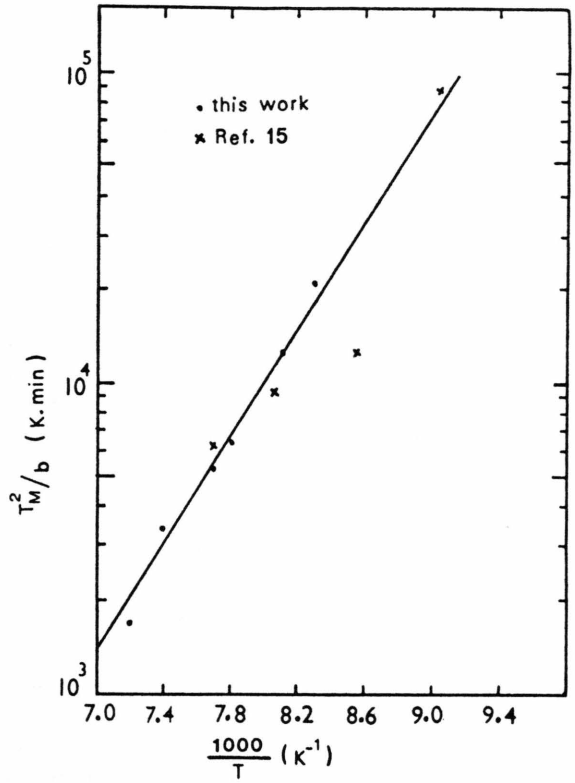

Fig. 4. Displacement versus heating rate of the low temperature DTC peak in ice. The drawn line represents a least-squares fit to the data.

ture. Then $\ln(T_M^2/b)$ varies linearly with $1/T_M$ with the slope W/k. This is shown in Fig. 4 for an ice sample. The heating rates were 0.7, 1.2, 2.5, 3.5, 5.2, 7.3 and 11.5 K/min. Also shown are experimental points measured by Johari and Jones [15] in polycrystalline ice Ih with heating rates 0.14, 1.10, 1.60 and 2.70 K/min. The straight line represents a least-squares fit to our data. From its slope a value of 0.17 eV was obtained for W. This is small compared with the value of 0.25 eV obtained from the ln I versus $1/T$ plot. The values for W obtained in this work from the variation of T_M with b were systematically considerably smaller than the values obtained from the ln I versus $1/T$ plots.

Discussion

Our results in polycrystalline ice Ih are to be compared with those of other investigators also in single samples: Johari and Jones [19] pointed out a) that the multiplicity of relaxation times in the orientation polarization at relatively low temperatures has been observed in single crystal ice Ih, polycrystalline ice Ih, Ic, III, V, VI VII and in ice clathrates and b) that the magnitude of the high frequency relaxation process is approximately the same for the polycrystalline and single crystal ice, although the concentration of physical defects is much higher in the former than in the latter. Also Chamberlain and Fletcher [20] observed similar behaviour in polycrystalline and single crystal samples by the DTC study of HF doped ice at low temperature.

The Variation of T_M with b

As mentioned above the values for the activation energy W obtained from the variation of the peak temperature T_M with heating rate b for the same sample were systematically considerably smaller than the values obtained from the plots of ln I versus $1/T$. Also measurements in oil-in-water (O/W) emulsions using the same experimental apparatus showed similar systematic deviations [21]. Also Kessler and Pflüger [22] observed such systematic deviations in DTC measurements in CdF_2:NaF. (The art of representation is somehow different.) It can be readily shown that a postulated positive difference between the electrode temperature (the quantity measured not only in our experiments but commonly) and the sample temperature (the quantity required) which increases with increasing b would explain this discrepancy. In a separate experiment the electrode temperature measured by a copper-constantan thermocouple attached to the upper (grounded) electrode was monitored against the real sample temperature measured by a second copper-constantan thermocouple frozen in the ice sample, when held at different steady temperatures and also when heated or cooled at different rates. The two temperatures measured with an accuracy of ±1 K were practically identical when held at a constant temperature in the range 85–250 K. When warming or cooling the electrode temperature was higher than the real sample temperature, the difference being larger for higher rates and lower temperatures. Thus the difference between the temperature measured in our DTC experiments (electrode temperature) and the real sample temperature is the origin for the lower values of W obtained from the variation of T_M with b. This difference does not influence significantly the value of $T_M = 125$ K reported in the Results section. In fact, if the sample was allowed to stand at 85 K for at least 10 minutes before warming was commenced, then for heating rates up to 4.0 K/min the difference between the two temperatures did not exceed 2 K in the range 85–250 K.

The Multiplicity of Relaxation Times

By the evaluation of W and τ_0 the assumption was made that the measured low temperature DTC peak is due to a single relaxation process described by Equation (1). Our experiments showed that this assumption presents only an approach, in agreement with Johari and Jones [15, 19] and in contrast to the results obtained by Jeneveau et al. [14]. This made itself evident in the impossibility to draw any straight line through the experimental points in the $\ln(P/I)$ versus $1/T$ plots and is also demonstrated in the discrepancy between the measured and the calculated DTC plots (Figure 3).

According to Johari and Jones [15, 19] likely three discrete relaxation processes contribute to the low temperature DTC peak in polycrystalline ice Ih. These authors, on the other hand, pointed out, that the results of the analysis into several discrete relaxation processes is somewhat ambiguous and that the low temperature polarization in ice may also be represented by a continuous distribution of relaxation times around a mean value. The multiplicity of relaxation times may be due to extrincis defects or to intrinsic ionic defects or to intrinsic orientation defects [19].

In order to study more accurately the multiplicity of the low-temperature DTC peak further experiments were performed. Firstly, the polarization temperature T_{p} was varied in the range between 20 K above and 20 K below the peak temperature T_{M}. If the low-temperature polarization in ice is represented by a continuous distribution of relaxation times around a mean value little or no variation in the shape of the DTC curve and especially in T_{M} would be observed by such a variation of T_{p}. In the case of several discrete relaxation processes it can be shown that lowering of T_{p} below T_{M} by suitable choice of the polarization time t_{p} may lead to a distortion in the shape of the DTC curve and a displacement of T_{M} to lower temperatures. Let us suppose with Johari and Jones [15] that two discrete relaxation processes mainly contribute to the low-temperature polarization in ice with nearly equal amplitudes and with relaxation times $\tau_1:\tau_2$ between 1:2 and 1:3. For $T_{\mathrm{p}} \gtrsim T_{\mathrm{M}}$ and $t_{\mathrm{p}} = 10$ min $> \tau_1(T_{\mathrm{M}}), \tau_2(T_{\mathrm{M}})$ the polarization due to each relaxation mechanism will reach its saturation value. Both processes contribute then nearly equally to the DTC curve. But for $T_{\mathrm{p}} < T_{\mathrm{M}}$ and $t_{\mathrm{p}} < \tau_1(T_{\mathrm{p}})$, $\tau_2(T_{\mathrm{p}})$ the degree of saturation is much different for the two relaxation mechanisms (the ratio $\tau_1:\tau_2$ will become also smaller). The process with the shorter relaxation time contribute then more to the DTC curve than the other one. This will cause a distortion in the shape of the DTC curve and a lowering of T_{M}. It is noteworthy that a variation of t_{p} alone is in principle sufficient for this experiment while a variation of both T_{p} and t_{p} is experimentally easier. It was not possible in our experiments to detect any variation in the shape of the DTC curve and any displacement of T_{M} by varying T_{p} and t_{p}, outside of the experimental errors. This favours the representation of the low temperature polarization in ice by a continuous distribution of relaxation times around a mean value.

In a second set of experiments an attempt was made to resolve the DTC curve into discrete peaks by partial discharging [17]. Several runs were made with each sample by varying the "cut" temperature. If a continuous distribution of relaxation times is assumed, the activation energy would increase systematically with increasing cut temperature. Also the temperature of the peak maximum T_{M} would increase slightly [23]. On the other hand, by two or three discrete relaxation processes it ought to be possible to separate reproducibly the corresponding peaks. It was not possible in our experiments to resolve the DTC curve reproducibly into two or three discrete peaks. On the contrary, the temperature of the peak maximum T_{M} increased systematically with increasing cut temperature. As far as the variation of the activation energy with increasing cut temperature is concerned, the accuracy in its determination was not sufficient enough for this to be proved.

Thus, the conclusion can be drawn that the low temperature DTC peak in ice may be better represented by a continuous distribution of relaxation times around a mean value than by a sum of single relaxation processes.

The Variation of T_{M} with Sample

Let us now return to the variation in the characteristics of the low temperature DTC peak for different samples measured in this work. The peak temperature T_M, that is the quantity directly measured in DTC experiments, is found to vary by as much as 6 K for different samples heated at the same rate. Johari and Jones [15] studying four different ice samples found T_M to vary by about 5 K and attributed this variation to the presence of varying concentration of extrinsic and the intrinsic orientational defects in ice. The observed variation of T_M with sample is probably the origin of the discrepancies in the values of T_M reported by different investigators.

Model for the Origin of the Low Temperature DTC Peak in Ice

A model for the origin of the low temperature DTC peak in ice has to take into account the following experimental results.

1) The peak has been found to be multiple (this work), in agreement with Johari and Jones [15].
2) Using the experimental possibilities offered by the DTC method we have found that the observed multiplicity may be better represented by a continuous distribution of relaxation times around a mean value than by a sum of single relaxation processes (this work). Accurate bridge measurements would be needed to prove this suggestion.
3) There is some experimental evidence that the peak is due to orientational polarization of water molecules in ice [15, 24].
4) The shape and the characteristics of the peak have been found to be independent of the purity of the water used in the conductivity range

$$1.1 \times 10^{-3}\ \mathrm{Ohm}^{-1} \cdot \mathrm{cm}^{-1} - 1.9 \times 10^{-6}\ \mathrm{Ohm}^{-1} \cdot \mathrm{cm}^{-1} \quad [24].$$

   From this it can be concluded that the shape and the characteristics of the peak are to some degree independent of the concentration of extrinsic chemical defects.
5) Similar dielectric behaviour has been observed in polycrystalline and single samples by the DTC study of HF doped ice at low temperatures [20]. Also a multiplicity of relaxation times at low temperatures has been observed in both polycrystalline [7, 15, 19] and single [8, 9] samples. In view of the fact that the former has a much higher concentration of physical defects than the latter, it could be concluded that the low temperature dielectric relaxation in ice is independent of the concentration of extrinsic physical defects. We think that further DTC experiments with both polycrystalline and single pure ice samples are needed for this conclusion to be proved.
6) The temperature of the peak maximum T_M has been found to vary by as much as 6 K for different samples heated at the same rate (this work), in agreement with Johari and Jones [15].

These results are consistent with a model already proposed [19]. In this model an intrinsic ionic defect interacts with the water molecules around it, with the result that the activation energy for the dipole reorientation for these water molecules is altered. The change in the activation energy decreases with increasing ion-water molecule distance. The change in the activation energy leads to a change in the relaxation time. Thus a distribution of relaxation times results from the ion-dipole interaction. The multiplicity of relaxation times in this model is to be considered as an intrinsic property of ice. The same effect may also be caused by the presence of impurity and/or physical defects in ice. In this case the multiplicity of relaxation times is to be considered as an extrinsic property. However, in view of the results No. 4 and 5 listed above the presence of impurity ions and/or physical defects can be excluded from being the origin of the observed multiplicity of relaxation times.

[1] D. Eisenberg and W. Kauzmann, The Structure and Properties of Water, Clarendon, Oxford 1969, p. 71.
[2] L. Pauling, J. Amer. Chem. Soc. **57**, 2680 (1935).
[3] N. Bjerrum, Kgl. Danske Videnskab. Selskab. Mat. Fys. Medd. **27**, No. 1 (1951).
[4] R. P. Auty and R. H. Cole, J. Chem. Phys. **20**, 1309 (1952).
[5] O. Wörz and R. H. Cole, J. Chem. Phys. **51**, 1546 (1969).
[6] R. Ruepp and M. Käss, in Physics of Ice, edited by N. Riehl, B. Bullemer, and H. Engelhardt, Plenum, New York 1969, p. 555.
[7] S. R. Gough and D. W. Davidson, J. Chem. Phys. **52**, 5442 (1970).

[8] A. Von Hippel, D. B. Knoll, and W. B. Westphal, J. Chem. Phys. **54**, 134 (1971).
[9] R. Ruepp, in Physics and Chemistry of Ice, edited by E. Whalley, S. J. Jones, and L. W. Gold, Royal Society of Canada, Ottawa 1973, p. 179.
[10] C. Jaccard, Phys. Kondens. Materie **3**, 99 (1964).
[11] H. Gränicher, in Physics of Ice, edited by N. Riehl, B. Bullemer, and H. Engelhardt, Plenum, New York 1969, p. 1.
[12] H. Engelhardt and N. Riehl, Phys. Lett. **14**, 20 (1965).
[13] A. Jeneveau and P. Sixou, Solid State Commun. **10**, 191 (1972).
[14] A. Jeneveau, P. Sixou, and P. Dansas, Phys. Kondens. Mater. **14**, 252, (1972).
[15] G. P. Johari and S. J. Jones, J. Chem. Phys. **62**, 4213 (1975).
[16] W. Kauzmann, Rev. Mod. Phys. **14**, 12 (1942).
[17] C. Bucci, R. Fieschi, and G. Guidi, Phys. Rev. **148**, 816 (1966).
[18] W. Squire, J. Comput. Phys. **6**, 371 (1970).
[19] G. P. Johari and S. J. Jones, Proc. Roy. Soc. London **A349**, 467 (1976).
[20] J. S. Chamberlain and N. H. Fletcher, Phys. Kondens. Mater. **12**, 193 (1971).
[21] P. Pissis, to be published.
[22] A. Kessler and R. Pflüger, J. Phys. C: Solid State Phys. **11**, 3375 (1978).
[23] R. D. Shelley and G. R. Miller, J. Solid Stat. Chem. **1**, 218 (1970).
[24] P. Pissis, L. Apekis, and G. Boudouris, to be published.