Multiplicity of Dielectric Relaxation Times of Dispersed Ice Microcrystals (*).

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Summary. — The multiplicity of relaxation times of the dielectric relaxation of water molecules in dispersed ice microcrystals has been studied by means of the thermally stimulated depolarization (TSD) current method. Using several experimental techniques offered by the TSD method we have shown that the relaxation mechanism is characterized by a continuous distribution of relaxation times with both the activation energy W and the pre-exponential factor τ_0 in the Arrhenius equation being distributed parameters. A linear relationship has been found to exist between W and $\ln \tau_0$. The dielectric behaviour of ice emulsions has been found to resemble strongly in some aspects that of HF-doped ice and ice samples with high concentrations of crystal imperfections. The multiplicity of relaxation times has been explained by the interaction of intrinsic ionic defects with water molecules.

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1. – Introduction.

Dispersions of ice microcrystals are obtained by the irreversible process of supercooling breakdown of water-in-oil type emulsions. Their dielectric properties have been studied by several investigators. At temperatures lower than about − 20 °C a dielectric relaxation in the kHz frequency range has been observed and attributed to dipolar absorption in ice [1-4]. The Cole-Cole

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[1] G. Evrard: in *Physics and Chemistry of Ice*, edited by E. Whalley, S. J. Jones and L. W. Gold (Royal Society of Canada, Ottawa, 1973), p. 199.
[2] B. Lagourette: *J. Phys. (Paris)*, **37**, 945 (1976).
[3] C. Lafargue, S. Bourgeois and G. Evrard: *J. Glaciol.*, **20**, 359 (1978).
[4] C. Boned, B. Lagourette and M. Clausse: *J. Glaciol.*, **22**, 145 (1979).

plot of this relaxation has been found to correspond to an arc of a circle indicating a distribution of relaxation times [1]. However, this distribution has not been studied any further.

This paper deals with a detailed study of the multiplicity of relaxation times of the dielectric relaxation of dispersed ice microcrystals due to dipolar absorption in ice. The experimental method used is the thermally stimulated depolarization (TSD) current method [5,6]. A major feature of the TSD method, which makes it particularly suitable for studying multiple dielectric relaxations, is that it offers the possibility to experimentally resolve relaxation processes arising from sets of dipoles with slightly different relaxation times [5,6].

Our interest in the dielectric properties of water-in-oil emulsions and dispersions of ice microcrystals is twofold: on the one hand, these relatively simple and easy to manipulate systems may serve as models for more complicated systems such as food emulsions and tissue; on the other hand, the comparison of the dielectric behaviour of dispersed ice microcrystals with that of macroscopic ice samples (of a few mm³ or more) could give us information useful to the understanding of the dielectric behaviour of ice at the molecular level.

2. – Experimental details.

The TSD method consists in studying the thermally activated release of stored dielectric polarization. The principle of the method is based on the exponential variation of the dipolar relaxation time τ with temperature T, which can be expressed by the Arrhenius equation

$$(1) \qquad\qquad \tau(T) = \tau_0 \exp\left[W/kT\right],$$

where W is the activation energy for dipolar reorientation, k is the Boltzmann constant and τ_0 is the so-called pre-exponential factor.

In TSD measurements the sample is polarized by applying an electric field E_p at some suitable polarization temperature T_p for a time t_p large compared to the relaxation time at T_p. With the electric field still applied, the sample is cooled down to a temperature T_0 sufficiently low to prevent depolarization by thermal energy. The field is then switched off and the sample is heated at a linear heating rate b. The resulting depolarization current is detected with the help of an electrometer.

In the case of a single-relaxation process the depolarization current density

[5] C. BUCCI, R. FIESCHI and G. GUIDI: *Phys. Rev.*, **148**, 816 (1966).
[6] J. VANDERSCHUEREN and J. GASIOT: in *Thermally Stimulated Relaxation in Solids*, edited by P. BRÄUNLICH (Springer-Verlag, Berlin, 1979), Chapt. 4.

$J(T)$ is given by [5,6]

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

where P_0 is the initial polarization. The maximum depolarization occurs at a temperature T_M,

$$(3) \qquad T_M = \left(\frac{bW\tau(T_M)}{k}\right)^{\frac{1}{2}}.$$

It is obvious from (2) that the TSD spectrum or thermogram (*i.e.* the plot of depolarization current *vs.* temperature) is an asymmetric peak (band) with the maximum depolarization current at T_M. It is also evident from (3) that T_M is independent of both the polarizing field E_p and the polarization temperature T_p, but depends upon the heating rate b.

The contribution of the TSD band to the static permittivity, $\Delta\varepsilon$, can be evaluated from

$$(4) \qquad \Delta\varepsilon = \frac{Q}{A\varepsilon_0 E_p},$$

where A is the cross-sectional area of the sample, ε_0 the permittivity of free space and Q the depolarization charge evaluated from the area enclosed in the spectrum,

$$(5) \qquad Q = \int_0^{\infty} J(t)\,\mathrm{d}t.$$

The activation energy W can be evaluated from the TSD spectrum in a number of ways. In this work W has been calculated by five different methods: the initial-rise method of Garlick and Gibson [7], the graphical-integration method of Bucci *et al.* [5], the simple Christodoulides formulae [8], the varying-heating-rate methods of Hoogenstraaten [9] and Prakash *et al.* [10] and the method of fitting the experimental data to the theoretical equation (2). By the initial-rise method, W is determined from the low-temperature tail of (2) using

$$(6) \qquad \ln J(T) = \text{const} - \frac{W}{kT}.$$

[7] G. F. J. GARLICK and A. F. GIBSON: *Proc. Phys. Soc.*, **60**, 574 (1948).
[8] C. CHRISTODOULIDES: *J. Phys. D*, **18**, 1501 (1985).
[9] W. HOOGENSTRAATEN: *Philips Res. Rep.*, **13**, 515 (1958).
[10] J. PRAKASH, RAHUL and A. K. NISHAD: *Phys. Status Solidi (a)*, **91**, 685 (1985).

The graphical-integration method uses the whole TSD spectrum to evaluate W. It can be shown that

$$(7) \qquad \ln\left|\frac{P(T)}{J(T)}\right| = \ln \tau(T) = \ln \tau_0 + \frac{W}{kT},$$

where $P(T)$, the polarization at temperature T, is obtained by graphical integration of the TSD spectrum. CHRISTODOULIDES [8] has proposed a number of approximate expressions for determining W of first-order peaks of thermoluminescence or TSD, using the widths or half-widths of the peaks. In this work we have used the expression

$$(8) \qquad W = \frac{T_1 T_2}{4738\,(T_2 - T_1)} - \frac{T_1}{11\,616},$$

where W is in eV and T_1 and T_2 denote the temperatures at which the current drops to half its maximum value on the low-temperature and high-temperature sides, respectively. The varying-heating-rate method of Hoogenstraaten [9] is based on the shift of the peak temperature T_M with heating rate b. By plotting $\ln(T_M^2/b)$ against $1/T_M$ a straight line is obtained, from the slope of which W can be calculated. By the varying-heating-rate method of Prakash et al. [10] the dependence of both current maximum I_M and peak temperature T_M on b is used. One gets a straight line when $\ln I_M$ is plotted against $1/T_M$. The slope of the straight line gives the value of W.

Using the method of least squares the values of W and T_M were determined giving the best fit of the theoretical equation (2) to the experimental peak. The height of the theoretical peak was taken to be the measured height. For each pair of energy value W and peak temperature T_M assumed, the sum of the squares of the differences between experimental and theoretical values of the current was estimated. The r.m.s. value S of these differences was taken as a measure of the goodness of fit of the theoretical to the experimental curve. A rough estimate for W was initially found using the approximate relation [8]

$$(9) \qquad W_0 = \frac{T_1 T_2}{4800\,(T_2 - T_1)}.$$

This was rounded to two significant figures. The approximate value of peak temperature T_{M0} was taken from the experimental curve, to within ± 0.5 K. The values of W examined ranged from $(W_0 - 0.05)$ to $(W_0 + 0.05)$ eV in steps of 0.01 eV and those of T_M from $(T_{M0} - 2)$ to $(T_{M0} + 2)$ K in steps of 0.5 K. For each of these $11 \times 9 = 99$ combinations of W and T_M values, the value of the figure of merit S was calculated. The best combination of W and T_M values was taken as that minimizing S.

By knowing the activation energy W, the pre-exponential factor τ_0 has been obtained from the equation

$$(10) \qquad \tau_0 = \frac{kT_M^2}{bW} \exp\left[-\frac{W}{kT_M}\right].$$

We used a homemade cryostat for measurements in the temperature range $(90 \div 300)$ K. The measuring capacitor was made of brass. The sample temperature was measured with a precalibrated copper-constantan thermocouple attached in close neighbourhood to the sample. The current was measured with a Keithley 610 C electrometer and recorded as a function of the temperature of the sample, with a YEW 3083 XY recorder. The temperature was controlled with a Barber-Colman 520 controller. The linear heating rate could be varied between 0.5 and 15.0 K/min. Typical values were 3 kV/cm for the polarizing field, 150 K for the polarization temperature, 5 min for the polarization time and 0.05 K/s for the heating rate. The uncertainties were ± 0.5 K in the peak temperature T_M, ± 0.01 eV in the activation energy W and a factor of about 2 in τ_0.

Our emulsions were supplied by l'Oreal (France). The volume fraction Φ of the dispersed water phase was 0.40 and 0.65. The ratio of the emulsifier volume (mainly zinc lanolate) to the volume of the emulsifier and oil (vaseline oil) was $\varrho \approx 0.3$. Microscopic observation revealed that the mean value of the diameter of the water droplets in the emulsions was about 2 μm and the distribution very narrow.

3. – Results and discussion.

TSD measurements in the temperature range $(85 \div 250)$ K on dispersions of ice microcrystals obtained by supercooling breakdown of water-in-oil emulsions with volume fractions Φ of the dispersed water phase 0.40 and 0.65 show, with brass electrodes, two predominant peaks: a low-temperature peak at 140 and 144 K, respectively, and a high-temperature peak at about 225 K ([11,12]). We have shown in a previous paper ([11]) that the low-temperature TSD peak and the dielectric relaxation observed in the kHz frequency range by many investigators using a.c. methods ([1-4]) are due to the same relaxation mechanism, namely the reorientation of water molecules in the ice microcrystals. Our initial goal of studying the multiplicity of relaxation times of the dielectric relaxation of dispersed ice microcrystals due to dipolar absorption in ice reduces

([11]) P. PISSIS, L. APEKIS, C. CHRISTODOULIDES and G. BOUDOURIS: *Z. Naturforsch. A*, **37**, 1000 (1982).
([12]) P. PISSIS, L. APEKIS, C. CHRISTODOULIDES and G. BOUDOURIS: *J. Chem. Phys.*, **87**, 4034 (1983).

to the study of the multiplicity of the low-temperature TSD peak. The properties of this peak were found to change with time, when after freezing at T_{fr} the emulsion was preserved at a constant temperature between T_{fr} and 0 °C ([11,12]) in agreement with a.c. studies ([1-4]). In this work our study is confined to samples without evolution in time, *i.e.* the samples were cooled down to the polarization temperature $T_p \leqslant 160$ K immediately after freezing.

3˙1. *Single or multiple peak?* – The following results show that the low-temperature TSD peak is multiple and the corresponding relaxation process distributed, in agreement with a.c. measurements ([1]):

1) Figure 1 shows the low-temperature TSD peak for the emulsion with $\Phi = 0.65$ together with the best fit of the theoretical equation (2) to this peak. It can be seen that the experimental curve cannot be fitted in a reasonable way by a curve given by (2), indicating that the peak is multiple and the corre-
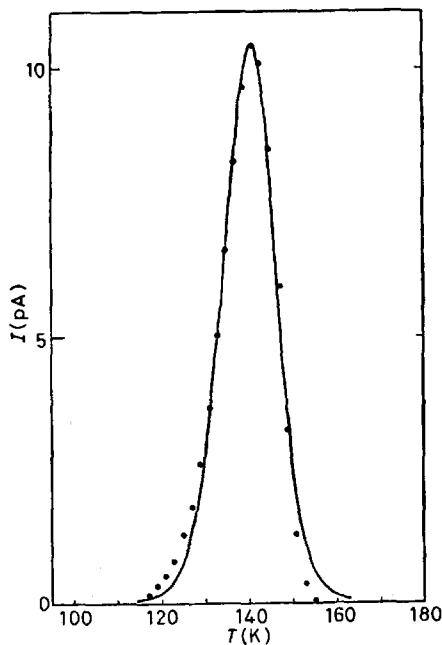

Fig. 1. – Low-temperature TSD peak in the emusion with $\Phi = 0.65$. • represents the fitting of (2) to the experimental data.

sponding relaxation process distributed. However, the experimental curve is practically not broader than the theoretical one and the discrepancies between the two curves are not serious in that temperature region in which the depolarization current is large, indicating that the distribution of relaxation times is rather narrow.

2) Table I lists values of the activation energy W of the low-temperature TSD peak for the emulsion with $\Phi = 0.40$ obtained by different methods. The discrepancies are larger than the experimental error of ± 0.01 eV. Even larger discrepancies result, if the same method is used on different parts of the experimental curve in calculating W, such as, for example, the use of the approximate expression using the temperatures at which the depolarization current is $\frac{1}{4}$ and $\frac{3}{4}$ of the peak height ([8]), either on the low-temperature or on the high-temperature side of the peak. These results are a strong indication that the low-temperature TSD peak is not single.

TABLE I. – *Values of the activation energy W of the low-temperature TSD peak for the emulsion with $\Phi = 0.40$ obtained by different methods.*

Method	W (eV)
initial-rise method, eq. (6)	0.36
graphical-integration method, eq. (7)	0.34
from temperatures of half-maximum current, eq. (8)	0.33
varying-heating-rate method (Hoogenstraaten)	0.34
varying-heating-rate method (Prakash)	0.35
least-squares fit	0.31

3) Figure 2 shows the low-temperature TSD peak for the emulsion with $\Phi = 0.40$ for two different polarization temperatures $T_p = 150$ and 130 K. With decreasing T_p, the peak was found to shift to lower temperatures. This shift is a powerful argument in favour of the existence of a distribution in relaxation times. Attention has been called to the fact that under certain conditions a similar dependence of T_M on T_p can be theoretically predicted for nondis-
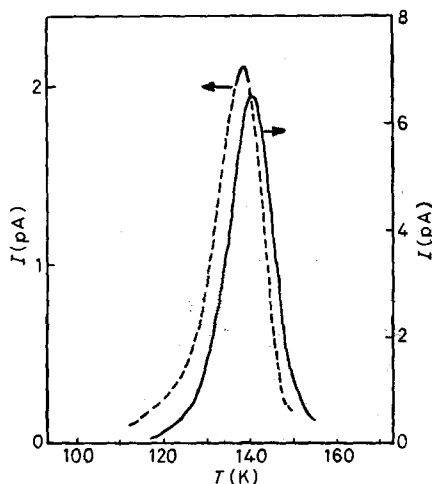

Fig. 2. – The low-temperature TSD peak in the emulsion with $\Phi = 0.40$ for two different polarization temperatures $T_p = 130$ K (– – –) and $T_p = 150$ K (———).

tributed peaks resulting from a space-charge polarization ([6]). However, it follows from our previous TSD measurements ([11,12]) and the a.c. measurements by other investigators ([1-4]) that the low-temperature TSD peak and the dielectric relaxation in the kHz frequency range in ice emulsions cannot possibly result from space-charge polarization.

3˙2. *Discrete or continuous distribution?* – The next question arising is whether the multiple low-temperature TSD peak is due to a discrete distribution in relaxation times, *i.e.* a superposition of two or more discrete single peaks, or a continuous distribution in relaxation times around a mean value. Our measurements provide evidence in favour of the existence of a continuous distribution:

1) A good indication that the peak may be better represented by a continuous distribution in relaxation times than by a sum of discrete peaks is provided by the fact that the shape of the peak does not change significantly with decreasing T_p, *i.e.* by suppressing the slow subpolarization (fig. 2).

2) In a set of experiments an attempt was made to resolve the low-temperature TSD peak into discrete peaks by partial discharging ([5,6]). By this technique, the temperature is increased in the step of depolarization to a point short of discharging the entire polarization and then dropped to its original value. Subsequent heating of the sample will now give a curve produced only by randomization of dipoles with the larger relaxation times of the distribution. Note that the techniques of varying the polarization temperature T_p and of partial discharging are complementary to each other, in the sense that the slow subpolarizations are suppressed by the first, while the fast subpolarizations are eliminated by the second. Several runs were made with each sample by varying the « cut » temperature T_c, *i.e.* the maximum temperature reached during the first temperature increase. If a continuous distribution of relaxation times is assumed, the temperature of the peak maximum T_M would increase systematically with increasing cut temperature, while the shape of the peak would practically not change with T_c. On the other hand, by two or three discrete relaxation processes it ought to be possible to separate reproducibly the corresponding peaks. Our experiments showed no evidence of the existence of discrete peaks. On the contrary, the peak temperature T_M was found to increase systematically with increasing cut temperature T_c (fig. 3), while the shape of the peak did not change significantly with T_c. This results support the hypothesis that the low-temperature TSD peak is characterized by a continuous distribution of relaxation times. Moreover, the activation energy W, calculated by the method of fitting the theoretical equation (2) to the experimental peak, was found to increase with increasing T_c. This is a first argument in favour of the existence of a distribution in activation energies.
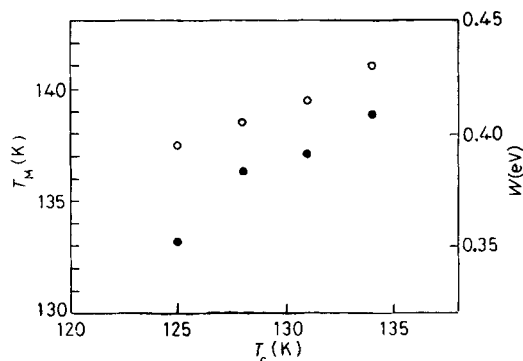
Fig. 3. – Peak temperature $T_M(\circ)$ and activation energy $W(\bullet)$ *vs.* cut temperature T_c in a series of partial-discharging experiments on the emulsion with $\Phi = 0.40$.

3) Overlapping TSD peaks may be separated by reducing the heating rate b [13]. Figure 4 shows the low-temperature TSD peak for the emulsion with $\Phi = 0.40$ for three different heating rates, $b = 0.030$, 0.067 and 0.142 K/s. Note that the peaks are normalized, *i.e.* the abscissa is depolarization current
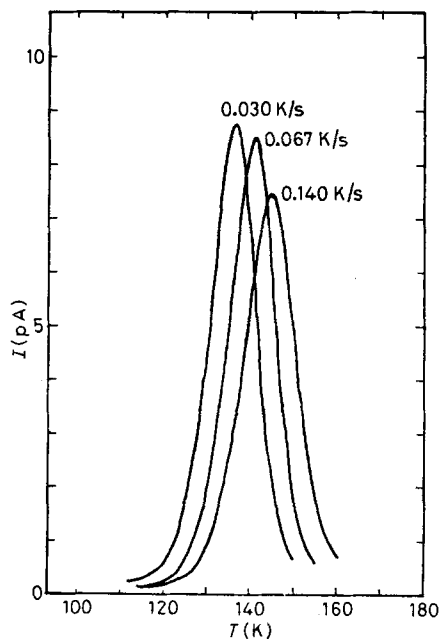

Fig. 4. – Normalized low-temperature TSD peak in the emulsion with $\Phi = 0.40$ for three different heating rates b.

[13] J. VAN TURNHOUT: *Thermally Stimulated Discharge of Polymer Electrets* (Elsevier, Amsterdam, 1975), Chapt. 2.

divided by heating rate. No changes, indicating that the peak consists of overlapping discrete peaks, were observed in the shape of the peak, when b was reduced to as low as 0.010 K/s. Heating the sample at lower rates was impracticable, since the current produced is then too low for precise measurements. These results indicate that the low-temperature TSD peak is characterized by a continuous distribution of relaxation times.

3.3. *Distribution in W or τ_0?* – Considering the Arrhenius equation (1), either the activation energy W or the pre-exponential factor τ_0, or both, may be distributed parameters. We investigated this question by using the thermal-sampling technique ([14-16]). This technique consists of « sampling » the relaxation process within a narrow temperature range by means of polarization at T_p followed by depolarization at T_d, a few K lower than T_p, in order to isolate some of the relaxation components. In a modification of the technique the sample was continuously cooled down at a constant rate of about 0.07 K/s and the polarizing field was switched on at T_p and switched off at T_d. The temperature window $T_p - T_d$ was 2 K. As an example, fig. 5 shows the low-
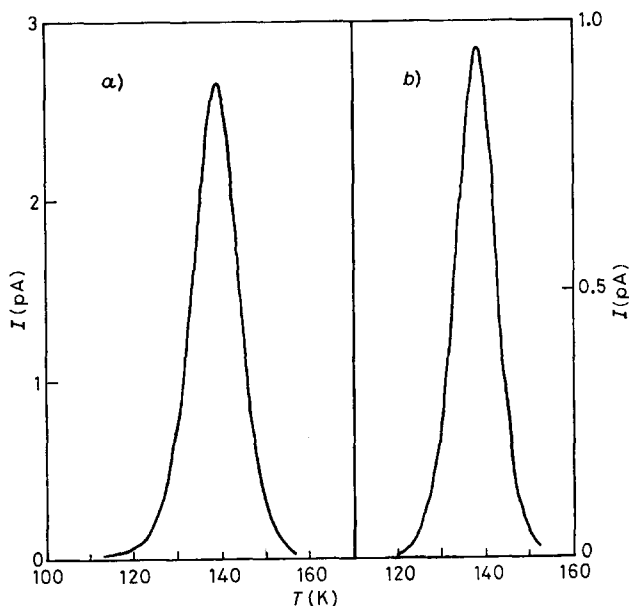

Fig. 5. – Low-temperature TSD peak in the emulsion with $\Phi = 0.40$ (a)) and a typical thermal sampling response isolated in this peak with $T_p = 139$ K, $T_d = 137$ K and $t_p = 30$ s (b)).

[14] T. HINO: *Jpn. J. Appl. Phys.*, **12**, 611 (1973).
[15] M. ZIELINSKI and M. KRYSZEWSKI: *Phys. Status Solidi* (*a*), **42**, 305 (1977).
[16] P. PISSIS, D. DIAMANTI and G. BOUDOURIS: *J. Phys. D*, **16**, 1311 (1983).

temperature TSD peak for the emulsion with $\Phi = 0.40$ and one of the thermal sampling responses isolated in this peak. The peak temperature T_M of these responses was found to increase systematically with increasing polarization temperature T_p (fig. 6). Moreover, the maximum of the responses could be
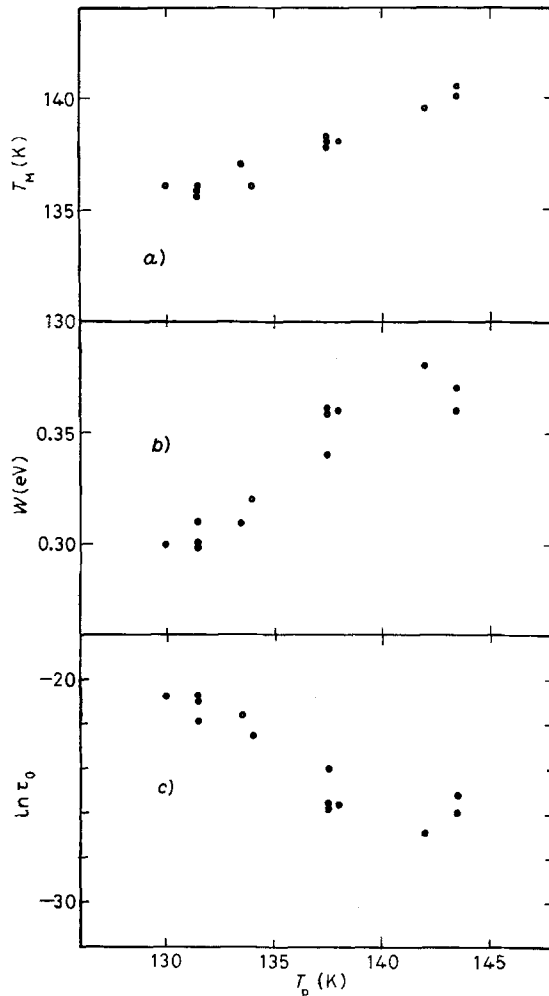

Fig. 6. – Peak temperature T_M (a)), activation energy W (b)) and logarithm of the pre-exponential factor $\ln \tau_0$ (c)) of the thermal-sampling responses isolated in the low-temperature TSD peak of the emulsion with $\Phi = 0.40$ *vs.* polarization temperature T_p.

situated anywhere in the temperature range of the original peak. These results provide further arguments in favour of the existence of a continuous distribution in relaxation times. The activation energy W of the thermal-sampling responses was calculated by the method of fitting the theoretical equation (2)

to the experimental peaks. The pre-exponential factor τ_0 was then obtained using (10). Figure 6 shows the dependence of W and $\ln \tau_0$ on T_p. With increasing T_p, W increases and τ_0 decreases systematically. Summarizing, our results show that the low-temperature TSD peak is multiple and the corresponding relaxation process continuously distributed, with both the activation energy W and the pre-exponential factor τ_0 in the Arrhenius equation being distributed parameters.
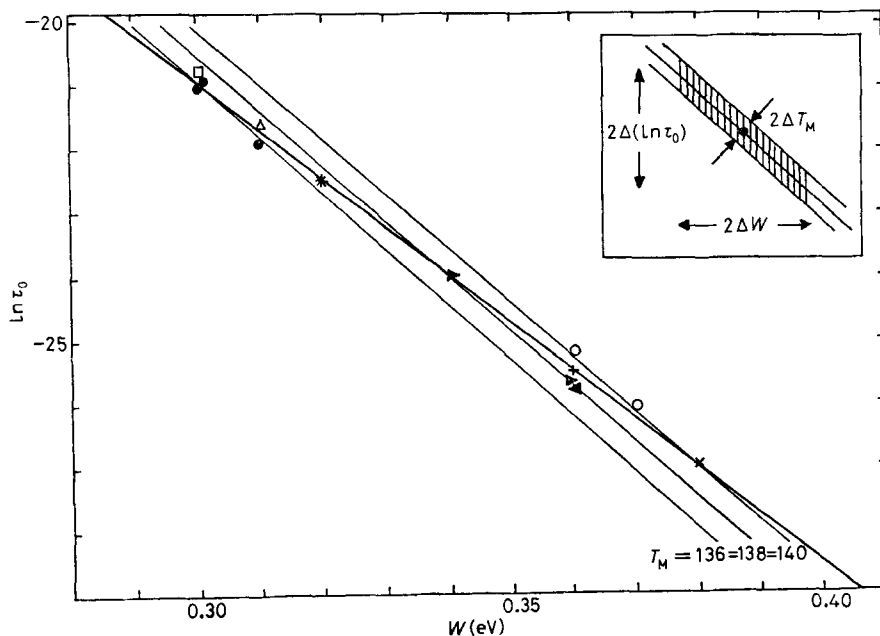

Fig. 7. – The relation between $\ln \tau_0$ and W of the thermal-sampling responses isolated in the low-temperature TSD peak of the emulsion with $\Phi = 0.40$. Also shown are three curves relating $\ln \tau_0$ to W for three peak temperatures T_M as found from the condition for peak maximum, eq. (10), for $b = 0.05$ K/s (thin lines). The inset shows how an uncertainty of ΔW in energy and ΔT_n in peak temperature result in an uncertainty $\Delta \ln \tau_0$ in $\ln \tau_0$ when the latter is determined using this equation. $T_p = 130$ (□), $T_p = 137.5$ (▲), $T_p = 131.5$ (●), $T_p = 138$ (+), $T_p = 133.5$ (▲), $T_p = 142$ (×), $T_p = 134$ (✱), $T_p = 143.5$ (○).

The dependence of W and $\ln \tau_0$ of the individual thermal-sampling responses on T_p, shown in fig. 6, suggests a relation between W and $\ln \tau_0$. Figure 7 shows a plot of $\ln \tau_0$ as a function of W. The best straight line passing through this set of data was found by the least-squares method (thick line). Assuming a relation of the form

$$(11) \qquad \ln \tau_0 = \ln \tau_0' - \frac{W}{\varepsilon},$$

it was found that $\tau_0' = 5.7$ s within a factor of 2 and $\varepsilon = (0.0132 \pm 0.003)$ eV with a coefficient of correlation $r = 0.997$. It must be borne in mind that the coefficients determined by this method are, in general, correlated in such a way as to result in straight lines passing between the experimental points and with deviations of experimental values from theoretical ones much smaller than the uncertainties in τ_0' and ε might suggest.

It was also verified that the linear relation between $\ln \tau_0$ and W in fig. 7 is a real and not an apparent one caused by the method used in determining τ_0 from (10), when W and T_M are known. The inset in fig. 7 shows the uncertainty in $\ln \tau_0$ resulting from those of W and T_M and the use of (10) in determining τ_0 from the values of W and T_M found from curve fitting. The central line in the inset is a plot of $\ln \tau_0$ as a function of W for the given T_M. It is seen that uncertainties of ΔW in W and ΔT_M in T_M result in a spread of the probable $\ln \tau_0$ values along the line (shaded region). For the experimental results presented, $\Delta W = 0.01$ eV and $\Delta T_M = 0.5$ K. It is possible, therefore, that, if experimental results for only a narrow range of T_M values are available, then a random distribution of the experimental points in the $\ln \tau_0 - W$ plot might appear as a systematic variation of $\ln \tau_0$ with W. To eliminate this possibility, the curves of $\ln \tau_0 - W$ from (10) (for $b = 0.05$ K/s) were compared to the straight line obtained from the experimental results. Three such lines are shown in fig. 7 for $T_M = 136$, 138 and 140 K (thin lines). The slopes of these lines, which are very nearly straight for the energies shown, are at $W = 0.35$ eV equal to 88.2, 87.0 and 85.8 1/eV, respectively, corresponding to energies of 0.0113, 0.0115 and 0.0117 eV. We see that these differ from the slope of the experimental straight line connecting $\ln \tau_0$ and W by more than five times the standard error in ε, which is 0.0003 eV. This fact, in addition to the systematic variation of W with T_p seen in fig. 6, is considered adequate proof that the correlation between $\ln \tau_0$ and W is real and not due to the method of data analysis used.

A linear relationship between W and $\ln \tau_0$ as shown in fig. 7 is known as compensation effect ([17,18]). The compensation effect has been revealed in many processes that require activation energy in order to proceed. The quantity ε in (11) is then usually written in the form $\varepsilon = kT_c$, where k is the Boltzmann constant and T_c the so-called compensation temperature. The physical meaning of the compensation temperature is still a subject of investigation and controversy ([18]). From $\varepsilon = (0.0132 \pm 0.0003)$ eV for the emulsion with $\Phi = 0.40$ we obtain $T_c = (155 \pm 4)$ K. It is noteworthy that $T_c = (156 \pm 5)$ K has been found for the dielectric relaxation of water molecules in frozen aqueous solutions of the monosaccharides glucose, mannose and galactose ([19]).

([17]) E. PEACOCK-LOPEZ and H. SUHL: *Phys. Rev. B*, **26**, 3774 (1982).

([18]) D. RONARC'H, P. AUDREN and J. L. MOURA: *J. Appl. Phys.*, **58**, 474 (1985).

([19]) D. DAOUKAKI-DIAMANTI, P. PISSIS and G. BOUDOURIS: *Chem. Phys.*, **91**, 315 (1984).

3˙4. *The relaxation mechanism in ice emulsions.* – We were able to show in a previous paper ([11]) that the low-temperature TSD peak and the dielectric relaxation observed in ice emulsions in the kHz frequency range by many investigators using a.c. methods ([1·4]) are due to the same relaxation mechanism, namely the reorientation of water molecules in the ice microcrystals. Moreover, based on our own and existing experimental results on ice emulsions, macroscopic pure ice, and macroscopic HF-doped ice and taking into account an explanation given by JOHARI and WHALLEY ([20]) for the temperature dependence of the activation energy W of the dielectric absorption in macroscopic pure and HF-doped ice, we could explain for the first time why, although the observed dielectric absorption in ice emulsions is generally attributed to dipolar absorption in ice, the emulsion activation energy is so much lower than that of macroscopic pure ice at temperatures higher than about -50 °C. Due to supercooling breakdown the concentration of extrinsic physical defects in ice emulsions is very high, so that extrinsically generated orientational defects dominate over the intrinsically generated ones in the whole temperature range, with the result that the activation energy of the dielectric relaxation is only due to the motion of the orientational defects (and not also to their formation). On the contrary, in macroscopic pure ice, extrinsically generated orientational defects dominate over the intrinsically generated ones at temperatures lower than about -50 °C, with the result that W changes from about 0.60 eV to about 0.25 eV as T drops below about -50 °C ([20]). This is the reason why the emulsion activation energy is so much lower than that of macroscopic pure ice at $T \geqslant -50$ °C.

The main result of the present study is that the dielectric relaxation of the water molecules in ice emulsions is characterized by a continuous distribution of relaxation times with both the activation energy W and the pre-exponential factor τ_0 being distributed parameters. In the case of the emulsion with $\Phi = 0.40$, W varies from 0.29 to 0.38 eV. These results have to be compared with corresponding results in macroscopic ice. TSD measurements on macroscopic polycrystalline pure ice show a low-temperature peak at 121 K, which is believed to result from the relaxation of water molecules ([12]). Thus the peak temperature T_M is about 20 K higher in ice emulsions than in macroscopic polycrystalline pure ice, indicating that the relaxation of water molecules is at low temperatures slower in ice microcrystals than in macroscopic ice. The low-temperature TSD peak in macroscopic ice has also been found to be multiple ([21]). Experiments to be published in due course suggest that the main mechanism contributing to this peak is characterized by a continuous distribution of relaxation times with probably both the activation energy W and

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([21]) P. PISSIS, G. BOUDOURIS, J. C. GARSON and J. L. LEVEQUE: *Z. Naturforsch. A*, **36**, 321 (1981).

the pre-exponential factor τ_0 being distributed parameters. The mean value of W is about 0.26 eV, *i.e.* about 0.08 eV lower than in ice microcrystals. However, W values close to our values in ice emulsions have been found also in other ice systems: 0.34 eV in HF-doped ice [22], 0.34 eV in ice crystals with high concentrations of crystal imperfections, created either by very rapid crystal growth or by traversing under pressure the phase transition ice Ih $\rightarrow$ $\rightarrow$ ice II $\rightarrow$ ice Ih [23] and 0.37 eV in ice samples prepared from the high-pressure forms ice II and ice IX [24]. The common feature of all these ice systems and of ice emulsions that makes them different from macroscopic polycrystalline pure ice is their high concentration of physical defects. Thus a possible explanation of the larger relaxation times and the higher activation energies in all these ice systems, compared to macroscopic polycrystalline pure ice, is that a higher activation energy is needed for the motion of the orientational D-and L-defects [20,21], because of the higher concentration of physical defects.

The dielectric properties of ice emulsions have been found to change with time, when after freezing at T_{fr} the emulsion was preserved at a constant temperature T_{pr} between T_{fr} and 0 °C [1,4,11,12]. The peak temperature T_M as well as the activation energy W have been found to decrease with increasing preservation temperature T_{pr} [11,12]. We think that it would be necessary for a better understanding of the dielectric relaxation mechanism in ice emulsions at the molecular level to study also its multiplicity at several stages of the evolution. This is at present being investigated in detail in our laboratory. We would like to remark in this connection that a similar evolution with time has been observed in the dielectric properties of ice samples with high concentrations of crystal imperfections [23,24]. Thus this is another point in which the dielectric behaviour of dispersed ice microcrystals resembles that of ice sample with high concentrations of crystal imperfections.

Our results show that in ice both the activation energy W and the pre-exponential factor τ_0 in the Arrhenius equation (1) are distributed parameters. A model consistent with these results is broadly speaking that of a defect interacting with the water molecules around it with the result that both the local concentration of the orientational D-and L-defects [20,21] and the energy needed for the motion of these defects is altered, the degree of change decreasing with increasing defect-water molecule distance. Thus a distribution of relaxation times results from the defect-water molecule interaction. The defects causing the multiplicity of relaxation times in this model may be intrinsic ionic defects [20,21] or extrinsic chemical and/or physical defects. In the first

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case the multiplicity of relaxation times is to be considered as an intrinsic property, while in the second case as an extrinsic property of ice. The existence of a multiplicity of relaxation times both in ice emulsions and macroscopic polycrystalline pure ice indicates that this multiplicity is, at least partly, an intrinsic property of ice. A detailed comparison of the characteristics of the multiplicity of relaxation times in ice emulsions and macroscopic polycrystalline pure ice is expected to be very useful regarding this question.

4. – Conclusions.

Our results show that the low-temperature TSD peak in ice emulsions and, thus, the dielectric relaxation of water molecules in dispersed ice microcrystals is multiple with both the activation energy W and the pre-exponential factor τ_0 in the Arrhenius equation being continuously distributed parameters. A linear relationship has been found to exist between W and $\ln \tau_0$. Both the peak temperature T_M and the mean value of W have been found to be higher in ice emulsions than in macroscopic polycrystalline pure ice, indicating that the relaxation mechanism is slower in the emulsions. Our own results and existing experimental results on several ice systems show that the dielectric behaviour of ice emulsions resembles that of macroscopic HF-doped ice and ice samples with high concentrations of crystal imperfections. In a model consistent with our results the multiplicity of relaxation times is explained by the interaction of water molecules with intrinsic ionic defects. However, further study is needed for a better understanding of the dielectric behaviour of ice emulsions at the molecular level. It would be particularly interesting to compare the characteristics of the multiplicity of relaxation times in ice emulsions at different stages of evolution with time with each other and with those of the multiplicity of relaxation times in macroscopic polycrystalline pure ice.

● RIASSUNTO (*)

La molteplicità dei tempi di rilassamento del rilassamento dielettrico di molecole d'acqua in microcristalli di ghiaccio dispersi è stata studiata col metodo della corrente di depolarizzazione stimolata termicamente (TSD). Usando le molte tecniche sperimentali offerte dal metodo TSD, si è mostrato che il meccanismo di rilassamento è caratterizzato dalla distribuzione continua dei tempi di rilassamento con sia l'energia di attivazione W che il fattore preesponenziale τ nell'equazione di Arrhenius come parametri distribuiti. Si è trovato che esiste una relazione lineare tra W e $\ln \tau_0$. Il comportamento dielettrico delle emulsioni di ghiaccio è stato trovato fortemente somigliante sotto alcuni aspetti a quello di ghiaccio marcato con HF e di campioni di ghiaccio con alte concentrazioni d'imperfezioni cristalline. La molteplicità dei tempi di rilassamento è stata spiegata con l'interazione di difetti ionici intrinsechi con molecole d'acqua.

Многозначность времен диэлектрической релаксации диспергированных монокристаллов льда.

Резюме (*). — С помощью метода термически стимулированной деполяризации исследуется многозначность времен диэлектрической релаксации молекул воды в диспергированных монокристаллах льда. Используя различную экспериментальную аппаратуру, мы показываем, что механизм релаксации характеризуется непрерывным распределением времен релаксации, причем энергия активации W и предэкспоненциальной множитель τ_0 в уравнении Аррениуса являюгся распреденными параметрами. Получено, что существует линейная связь между W и $\ln \tau_0$. Обнаружено, что диэлектрическое поведение эмульсий льда напоминает диэлектрическое поведение льда с примесями HF и льда с высокими концентрациями дефектов кристаллической решетки. Многозначность времен объясняется взаимодействием внутренних ионных дефектов с молекулами воды.

(*) *Переведено редакцией.*