

# DIELECTRIC BEHAVIOUR OF DISPERSE ICE MICROCRYSTALS IN THE FREQUENCY RANGE $10^5$ TO $10^{-2}$ Hz

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**ABSTRACT.** Dielectric properties of ice microcrystals have been studied in the frequency range  $3 \times 10^5$  to  $10^{-2}$  Hz. Two separated dispersions are revealed: the Debye dispersion of ice and another dispersion at very low frequencies. Both dispersions present an ageing effect, with decreasing activation energy for the Debye dispersion and with increasing activation energy for the second one. It is shown in this paper that the sum of these activation energies retains a constant value of  $(1.05 \pm 0.02)$  eV.

**RÉSUMÉ.** Comportement diélectrique de relaxation de micro-cristaux de glace dans les gammes de fréquences de  $10^5$  et  $10^{-2}$  Hz. Les propriétés diélectriques de micro-cristaux de glace se présentent sous la forme de deux domaines disjoints de relaxation: la relaxation Debye de la glace aux fréquences acoustiques, et une seconde relaxation aux très basses fréquences. Les deux relaxations sont le siège d'une évolution qui se traduit notamment par une diminution de l'énergie d'activation Debye et par une augmentation de l'énergie d'activation de la seconde relaxation. On montre que la somme des deux énergies d'activation garde une valeur constante de  $(1,05 \pm 0,02)$  eV.

**ZUSAMMENFASSUNG.** Das dielektrische Verhalten disperser Eis-Mikrokristalle im Frequenzbereich  $10^5$ - $10^{-2}$  Hz. Die dielektrischen Eigenschaften von Eis-Mikrokristallen wurden im Frequenzbereich von  $3 \times 10^5$ - $10^{-2}$  Hz untersucht. Es lassen sich zwei verschiedene Dispersionen feststellen: die Debye-Dispersion von Eis und eine weitere Dispersion bei sehr niedrigen Frequenzen. Beide Dispersionen weisen einen Alterungseffekt auf, wobei die Aktivierungsenergie bei der Debye-Dispersion ab-, bei der zweiten Dispersion jedoch zunimmt. Es lässt sich zeigen, dass die Summe dieser Aktivierungsenergien den konstanten Wert  $(1,05 \pm 0,02)$  eV einhält.

## INTRODUCTION

For many years, research on dielectric properties of ice has mainly dealt with monocrystals in order to limit experiments to well-defined samples. One may yet wonder whether the microtoming of the samples does not alter the bulk structure of ice. On the other hand, experiments on doped ice have been chiefly conducted with a view to checking the theories on the electrical properties of ice.

A different orientation has lately been tried. With a view to giving glaciologists a better understanding of polar and temperate glacier ice, polycrystalline ice has been systematically studied. Furthermore, the fact that snow crystals are formed by the freezing of supercooled water down to as low as  $-41^\circ\text{C}$ , in itself accounts for the interest shown in the study of frozen emulsions of water in oil.

Lafargue (unpublished) has presented evidence for the existence of discrete temperatures at which supercooled water freezes given by the formula  $T_n = (-164^\circ\text{C})/n$  ( $n$  an integer  $4 \leq n \leq 10$ ). These temperatures, which do not seem to be dependent on environment and impurities (except ice isomorphs), seem to be related with the structure of the liquid. Whereas the probability of a droplet freezing is dependent on volume, impurities, and, in a complex way, on environment.

Remarkable changes of the dielectric behaviour occur during the ageing of micron-sized droplets formed when emulsions of supercooled water freeze at  $-41^\circ\text{C}$ . During the ageing, the activation energy of the relaxation frequency falls from 0.58 eV immediately after freezing to as low as 0.16 eV in a way that maintains stable the relaxation frequency at  $0^\circ\text{C}$ . Certain activation energy values are more likely to occur depending on the age and storage temperature. These values form a discrete sequence  $U_n = (-0.042 + 0.069n)$  eV where  $n$  is an integer (Evrard, 1973); intermediate values always occur before reaching a plateau, sometimes after  $10^3$  h or even more. Very similar results have been obtained with pure polycrystalline ice (Boned and Barbier, 1973). Some of the values of this sequence seem to have

been seen also by Fitzgerald and others (1977) on polar ice and on finely grained ice microcrystals. These more likely values have been shown to be related to the more likely temperatures of supercooling breakdown (Evrard, 1973). As compared to polycrystalline ice, disperse microcrystals present a twofold interest: on the one hand, they make it possible to study crystals formed, much like snow, by the freezing of highly supercooled water, on the other hand emulsions present no d.c. conductivity. For this reason, they can be studied in a very wide frequency range, e.g.  $10^{10}$  Hz to  $10^{-3}$  Hz. In the case of polycrystalline ice, d.c. conductivity can conceal possible very low frequency (V.L.F.) dispersions.

This paper presents results of the study of dielectric properties of disperse ice microcrystals in the frequency range  $10^5$  Hz to  $10^{-2}$  Hz obtained with two different devices. A type 716 C General Radio Capacitance Bridge was used in the frequency range  $3 \times 10^5$  to  $10^3$  Hz. Capacitance and dissipation factor are measured by the substitution method, both for the empty cell and for the cell with the sample.  $\epsilon'$  and  $\epsilon''$  are deduced with an accuracy  $\Delta\epsilon'/\epsilon' \approx \Delta\epsilon''/\epsilon'' \approx 0.01$ . In the frequency range  $10^4$  to  $10^{-2}$  Hz, a type 1172 Schlumberger frequency-response analyser was used. The cell is excited by a high-stability sinusoidal output  $V_x$ . The resulting amplitude and phase output of the cell  $V_y$  is analysed in the form  $V_y/V_x = a + jb$  with an accuracy of  $10^{-4}$  for  $\Delta a/a$  and for  $\Delta b/b$ .  $\epsilon'$  and  $\epsilon''$  are deduced from the values of  $a$  and  $b$  both for the empty cell and for the cell with the sample, with an accuracy  $\Delta\epsilon'/\epsilon' \approx \Delta\epsilon''/\epsilon'' \approx 0.01$ . Values obtained by the two devices in the common frequency range are consistent. The sample was stored in a CS 601 type "Ferisol" Dielectric Cell with the "35 pF" electrode.

Ice was obtained by supercooling breakdown at  $-41^\circ\text{C}$  of droplets of water a few microns in diameter in an emulsion of water in oil. The oil phase was a lanolin-paraffin oil mixture with 0.05 lanolin by weight.

#### EXPERIMENTAL RESULTS

We have studied one sample of ice of weight fraction  $P = 0.45$  (sample a), and two different samples of ice of weight fraction  $P = 0.40$  (samples b and c); for all samples, the results are identical. In this paper, the curves relate to sample a, although some numerical values are reported for the other samples. The complex dielectric constant of disperse ice microcrystals is shown to traverse two separate dispersions (Fig. 1). The first one, at audio frequencies, is due to the Debye dispersion of ice; the second one occurs at V.L.F.

An ageing effect is observed, which is greater at the highest storage temperatures. When a sample has been stored at a given temperature ( $-1^\circ\text{C} > \theta > -41^\circ\text{C}$ ) for about 20–40 h, so that the evolution at this temperature becomes extremely slow, it is first measured at this

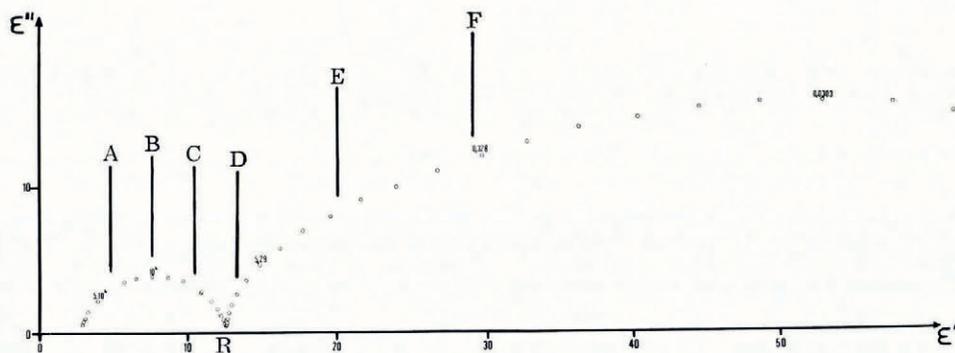


Fig. 1. Complex dielectric constant of disperse ice microcrystals in the frequency range  $10^5$  to  $10^{-2}$  Hz. Temperature  $-24^\circ\text{C}$ .  $P = 0.45$ . The meeting point R of the two dispersions is the point where  $\epsilon''$  is minimum.

temperature and then measured again at other temperatures  $T < \Theta$ , no further evolution being observed whenever  $T \leq \Theta$ . This set of measurements is therefore characteristic of the stage of the evolution at the storage temperature  $\Theta$ . The sample is then heated and maintained at a storage temperature  $\Theta' > \Theta$ . A further evolution is observed and measured at some temperatures  $T' \leq \Theta'$ , and so on for increasing storage temperatures.

The strength of both dispersions depends on the weight fraction  $P$  of the ice in the emulsion, and on the storage temperature. For a given temperature  $\Theta$ , the strength of both dispersions is not very temperature dependent (Figs 2 and 3).

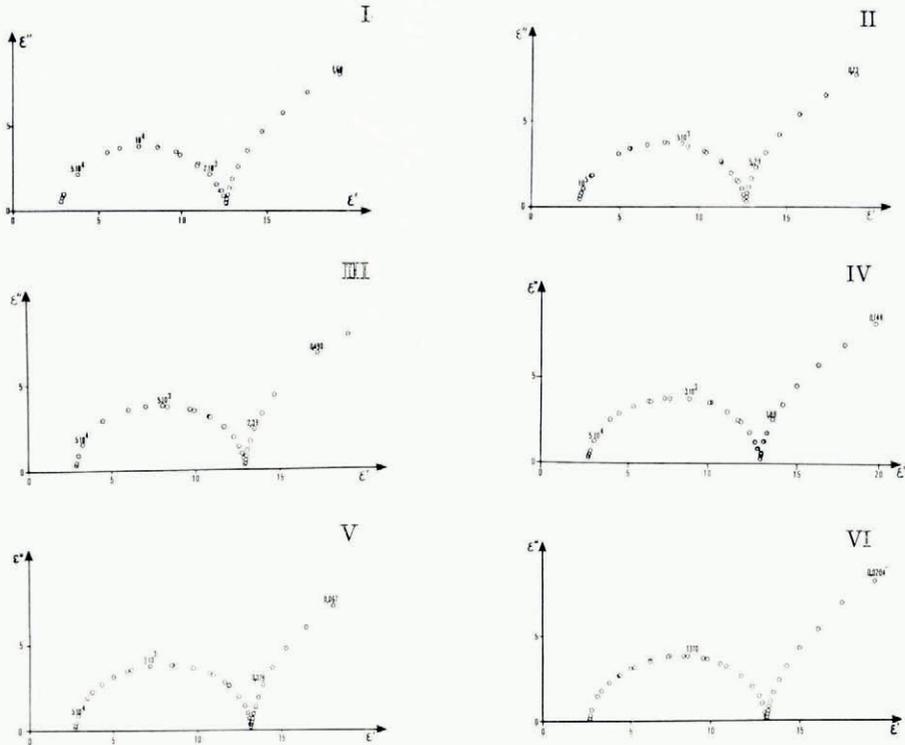


Fig. 2. Audio-frequency dispersion as a function of temperature for a given preserving temperature.  $\Theta = -19.3^{\circ}\text{C}$ .  $P = 0.45$ .

- I.  $T = -24.0^{\circ}\text{C}$ . II.  $T = -29.6^{\circ}\text{C}$ . III.  $T = -34.0^{\circ}\text{C}$ .
- IV.  $T = -34.0^{\circ}\text{C}$ . V.  $T = -45.7^{\circ}\text{C}$ . VI.  $T = -51.1^{\circ}\text{C}$ .

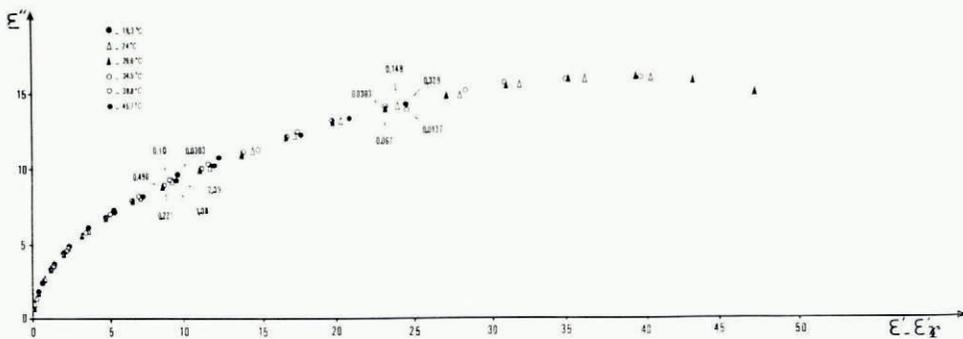


Fig. 3. V.L.F. dispersion as a function of temperature.  $P = 0.45$ .  $\Theta = -19.3^{\circ}\text{C}$ .

$\epsilon_{\infty}$ , the value of  $\epsilon'$  for metre waves, does not depend on temperature.  $\epsilon_R$ , the value of  $\epsilon'$  at the meeting point R (see Fig. 1), is slightly temperature dependent:  $\partial\epsilon_R/\epsilon_R \partial T \approx 1.5 \times 10^{-3} \text{ K}^{-1}$  between  $-10^\circ\text{C}$  and  $-50^\circ\text{C}$  for all samples. The strength of the second dispersion does not depend on temperature, as shown in a diagram of  $\epsilon' - \epsilon_R$  against  $\epsilon''$ . All the experimental values lie on a master curve (Fig. 3).

To get the temperature dependence of the frequency for both dispersions, we have plotted three points on each dispersion curve (Fig. 1) A, B, and C for the first dispersion, refer to fixed values of  $\epsilon'/(\epsilon_R - \epsilon_{\infty})$ . In this way, B is shown to refer to the maximum of  $\epsilon''$ . D, E, and F for the second dispersion, refer to fixed  $\epsilon' - \epsilon_R$  values, because of the existence of the master curve (Fig. 3). R is the meeting point, where  $\epsilon''$  is at a minimum. For all samples, the frequency associated with each point depends on temperature according to an Arrhenius-type law. A common value of activation energy is observed for A, B, and C (first dispersion), and another common value for D, E, and F (second dispersion). These values depend on the storage temperature  $\Theta$ , i.e. the stage of the evolution (Fig. 4, Table I). Figure 5 refers to the meeting-point activation energy.

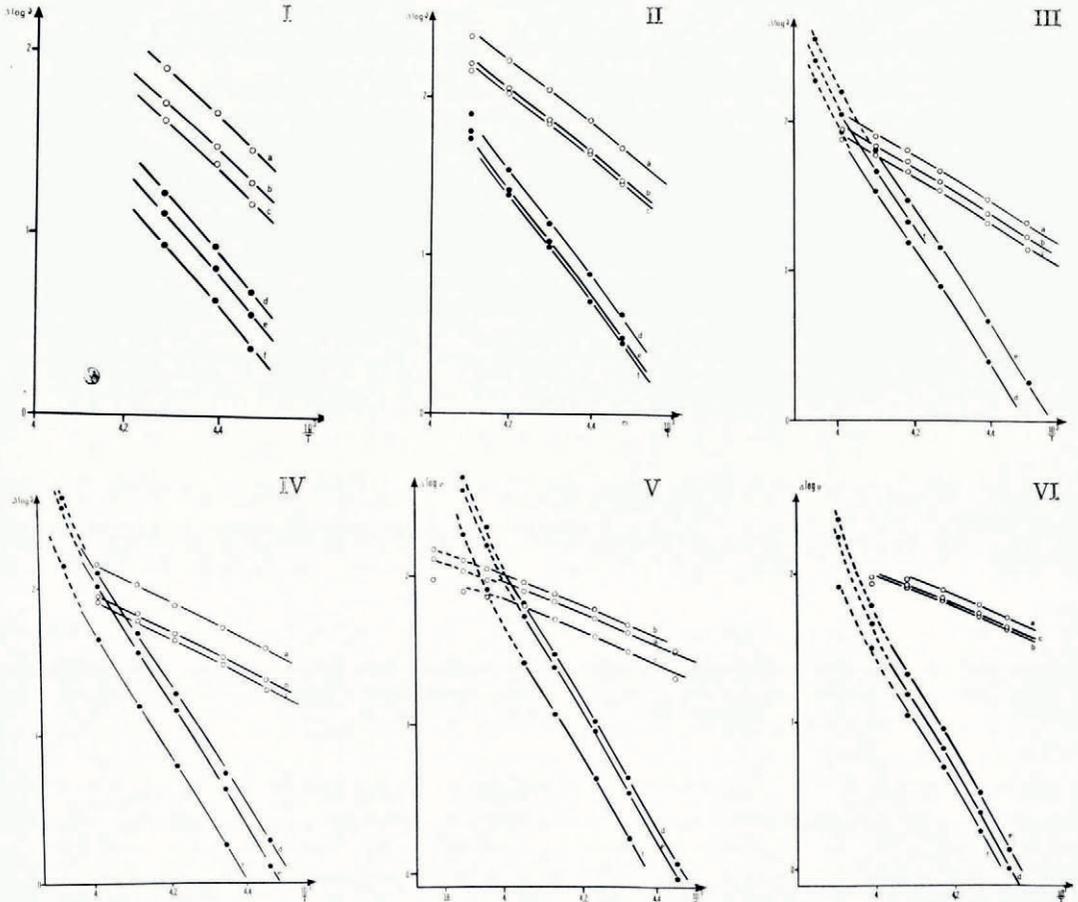


Fig. 4. Temperature dependence of the frequencies related to the points A, B, C, D, E, F (see Fig. 1). Frequency is obtained by:  $\log v = K + \Delta \log v$  (see Table I).  $P = 0.45$ .

I.  $\Theta = -39.5^\circ\text{C}$ . II.  $\Theta = -29.4^\circ\text{C}$ . III.  $\Theta = -19.3^\circ\text{C}$ .  
IV.  $\Theta = -11.8^\circ\text{C}$ . V.  $\Theta = -6.6^\circ\text{C}$ . VI.  $\Theta = -1.1^\circ\text{C}$ .

TABLE I. VALUES OF  $K$  RELATED TO THE FREQUENCIES IN FIGURE 4

	I	II	III	IV	V	VI
a	2.0	2.0	2.5	2.5	3.0	2.8
b	1.5	1.5	2.0	2.0	2.0	2.0
c	1.0	1.0	1.5	1.5	1.5	1.5
d	-0.5	-1.0	-1.0	-1.5	-1.5	-1.5
e	-1.0	-1.5	-2.0	-2.0	-2.0	-2.0
f	-1.5	-2.0	-2.5	-2.5	-2.0	-2.0

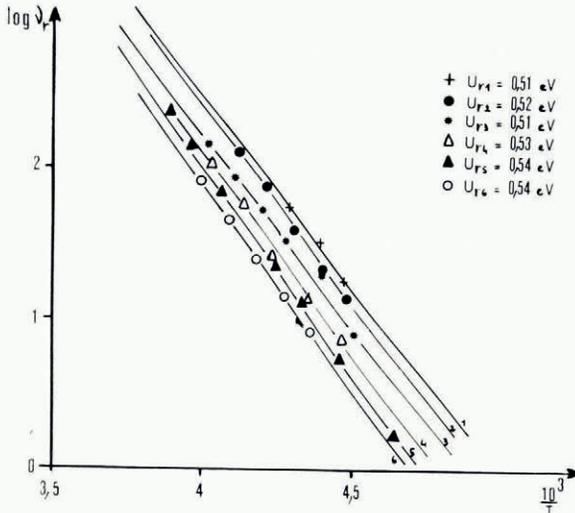


Fig. 5. Temperature dependence of the frequency  $\nu_R$  related to the meeting point  $R$ .  $P = 0.45$ .

- 1.  $\Theta = -39.5^\circ\text{C}$ .
- 2.  $\Theta = -29.4^\circ\text{C}$ .
- 3.  $\Theta = -19.3^\circ\text{C}$ .
- 4.  $\Theta = -11.8^\circ\text{C}$ .
- 5.  $\Theta = -6.6^\circ\text{C}$ .
- 6.  $\Theta = -1.1^\circ\text{C}$ .

Let  $U_I$  be the audio-frequency dispersion activation energy,  $U_{II}$  the V.L.F. dispersion activation energy, and  $U_R$  the meeting-point activation energy; it can be noticed that  $U_I$  decreases and  $U_{II}$  increases with increasing preserving temperatures. Conversely  $U_R$  remains constant. Table II gives the values of activation energies for samples a and b. It can be noticed that the values of  $U_I$  are not necessarily close to one of the values of the sequence  $U_n = (-0.042 + 0.069n)$  eV. This can naturally occur because the sample has not been stored long enough to reach a plateau value.

It is shown in Table II that the values of  $U_I$  are correlated with those of  $U_{II}$ . The sum  $U_I + U_{II}$  retains a constant value which is the same for both samples, about 1.05 eV. It must be noticed that sample c, which has been stored for four months at  $-1^\circ\text{C}$ , presents the following values:  $U_I = 0.17$  eV,  $U_{II} = 0.91$  eV,  $U_I + U_{II} = 1.08$  eV, and  $2U_R = 1.05$  eV. The fact that  $U_I + U_{II}$  keeps a constant value during the ageing, seems to point to the existence of more likely values of  $U_{II}$  corresponding to plateaux. A study of the evolution will be necessary to confirm this result.

One can also see that  $U_R$  retains a constant value during the ageing and that this value is precisely  $U_R = \frac{1}{2}(U_I + U_{II})$ . This fact is easy to explain. If we write for the melting point

$$\omega\tau_1 \ll 1 \ll \omega\tau_2,$$

TABLE II. ACTIVATION ENERGIES

<i>Sample a</i>				
$\Theta$ °C	$U_I (\pm 0.01)$ eV	$U_{II} (\pm 0.01)$ eV	$U_I + U_{II} (\pm 0.02)$ eV	$2U_R (\pm 0.02)$ eV
-39.5	0.46	0.57	1.03	1.02
-29.4	0.39	0.66	1.05	1.04
-19.3	0.30	0.76	1.06	1.03
-11.8	0.26	0.82	1.08	1.06
-6.6	0.22	0.86	1.08	1.09
-1.1	0.21	0.86	1.07	1.08
<i>Sample b</i>				
$\Theta$ °C	$U_I (\pm 0.01)$ eV	$U_{II} (\pm 0.01)$ eV	$U_I + U_{II} (\pm 0.02)$ eV	$2U_R (\pm 0.02)$ eV
-40.6	0.50	0.54	1.04	1.00
-24.0	0.32	0.73	1.05	1.06
-5.0	0.23	0.80	1.03	1.08

and if the approximation is made that the dispersions are of the simple Debye type of strengths  $\Delta\epsilon_1$  and  $\Delta\epsilon_2$  which are temperature-independent, then the angular frequency corresponding to the minimum,  $\omega_R$ , satisfies

$$\omega_R^2 = (\Delta\epsilon_2/\Delta\epsilon_1)(\tau_1\tau_2)^{-1}.$$

Thus  $\omega_R$  should have an activation energy of  $\frac{1}{2}(U_I + U_{II})$ .

This accounts for the agreement of  $2U_R$  with  $U_I + U_{II}$ . (This result remains valid even if the dispersions are not of the simple Debye type provided the relaxation times of each dispersion have the same activation energy). If the two dispersions are such that  $\Delta\epsilon_1/\tau_1 > \Delta\epsilon_2/\tau_2$ , the product  $\sigma_0\sigma_\infty$  for the dispersion I has magnitude  $\epsilon_0^2\Delta\epsilon_1\Delta\epsilon_2/\tau_1\tau_2$ . With the same approximations as above, the activation energy for  $\sigma_0\sigma_\infty$  is  $U_I + U_{II}$  which would again be a constant. The observations of Camp and others (1969) and Camplin and Glen (1973) of a nearly constant value for the activation energy of  $\sigma_0\sigma_\infty$  is therefore of great relevance. Camplin and Glen (1973) found in single crystals of HF-doped and pure ice, activation energies between 0.49 eV and 0.61 eV for  $\sigma_0\sigma_\infty$ , the mean value being 0.535 eV. Our values in microcrystals for  $U_I + U_{II}$  lie between 1.02 and 1.09 eV, and the mean value is 1.05 eV. It is most interesting that the mean values differ by just a factor of two.

## CONCLUSION

It is noteworthy that the two dispersions that occur in ice microcrystals present, during the ageing, activation energies whose sum retains a constant value. The more likely values of activation energy for the high-frequency dispersion had already been shown to be related to the more likely temperatures of breakdown of water supercooling. Activation energies for the low-frequency dispersion should therefore also have more likely values corresponding to plateaux. In spite of the difficulties involved, this evolution would be worth studying.

Work up to date does not enable us to understand the complete mechanism of the V.L.F. dispersion. A numerical analysis with a computer, and additional experiments on pure polycrystalline ice are now in progress.

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## REFERENCES

- Boned, C., and Barbier, A. 1973. A study of the change with time of the dielectric properties of polycrystalline ice. (In Whalley, E., and others, ed. *Physics and chemistry of ice: papers presented at the Symposium on the Physics and Chemistry of Ice, held in Ottawa, Canada, 14-18 August 1972*. Edited by E. Whalley, S. J. Jones, L. W. Gold. Ottawa, Royal Society of Canada, p. 208-11.)
- Camp, P. R., and others. 1969. Electrical conduction in ice, [by] P. R. Camp, W. Kiszynick, D. Arnold. (In Riehl, N., and others, ed. *Physics of ice: proceedings of the international symposium on physics of ice, Munich, Germany, September 9-14, 1968*. Edited by N. Riehl, B. Bullemer, H. Engelhardt. New York, Plenum Press, p. 450-70.)
- Camplin, G. C., and Glen, J. W. 1973. The dielectric properties of HF-doped single crystals of ice. (In Whalley, E., and others, ed. *Physics and chemistry of ice: papers presented at the Symposium on the Physics and Chemistry of Ice, held in Ottawa, Canada, 14-18 August 1972*. Edited by E. Whalley, S. J. Jones, L. W. Gold. Ottawa, Royal Society of Canada, p. 256-61.)
- Evrard, G. 1973. Changes in the dielectric properties of ice formed by supercooling breakdown. (In Whalley, E., and others, ed. *Physics and chemistry of ice: papers presented at the Symposium on the Physics and Chemistry of Ice, held in Ottawa, Canada, 14-18 August 1972*. Edited by E. Whalley, S. J. Jones, L. W. Gold. Ottawa, Royal Society of Canada, p. 199-203.)
- Fitzgerald, W. J., and others. 1977. Are the anomalous dielectric properties of polar ice due to impurities? [By] W. J. Fitzgerald, J. W. Glen and J. G. Paren. [*Union Géodésique et Géophysique Internationale. Association Internationale des Sciences Hydrologiques. Commission des Neiges et Glaces.*] *Symposium. Isotopes et impuretés dans les neiges et glaces. Actes du colloque de Grenoble, août/septembre 1975*, p. 3-8. (IAHS-AISH Publication No. 118.)
- Lafargue, C. Unpublished. Les limites de stabilité de l'eau surfondue. [Doctorat d'Etat thesis, Université de Paris, 1952.]