Electrical Conductivity of the Surface Layer of Ice

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Abstract

The DC electrical conductivity of freshly cut ice surfaces has been measured at $-11°C$ in two different ways: a four-point method applied to a thin circular sample, and two-point resistance measurements on meander-like samples taken at decreasing thicknesses. Both methods indicate a surface conductivity for pure ice in the order of 10^{-10} ohm^{-1}, thus making the surface electrically equivalent to a bulk layer with a thickness of 1 to 4 mm. The surface resistance is not influenced by a perpendicular electric field, but it is decreased by about 20% in an air current. The time dependence of the transient behavior when the air stream is turned on and off is not symmetrical and seems to indicate a trap mechanism for the charge carriers in the surface layer. A simple qualitative model attributes tentatively the surface conductivity to the positive ions H_3O^+; they are trapped by superficial L-defects, which are removed during sublimation in the air current.

I. Introduction

The surface layers of ice crystals have physical properties which seem to differ considerably from those of the bulk. Results of mechanical experiments by Nakaya (1954) and by Jellinek (1961) have been explained by the existence of a liquid-like layer. In a theoretical investigation, Fletcher (1962) assumes a highly polarized structure of the surface with the negative molecular vertices outward. A disorderd zone extends to the bulk, where the molecules are coordinated in a regular tetrahedral way, and the protons are distributed on the bonds according to the Bernal-Fowler rules (1933).

The hypothesis of a particular surface structure and behavior is supported by the experiments reported below, which reveal a DC electrical surface conductivity much higher than in the bulk. The methods of measurement and their results are first described, then the effects of external agents such as an electric field and an air current are noted; the observed phenomena are discussed in the last section.

II. Measurement of the Surface Conductivity

Four-point method. A method has been described by Schnabel (1964) to measure two components of the electric resistivity tensor in a thin, flat specimen. We attempted to apply it to ice to determine the anisotropy of the DC conductivity, but the results were incompatible with the formulas. However, the discrepancy can be explained by the occurrence of a large surface conductivity and the original theory has been modified in this sense (Jaccard, 1966). The measurement principle is as follows (Fig. 1): An ice

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$$\left(V_{BD}/J_{AC}\right)\cdot\Pi w\,\sigma_{v} = G(s/w)+(\sigma_{s}/\sigma_{v}w)\cdot G_{1}(s/w)$$

$$\left(V_{CD}/J_{AB}\right)\cdot\Pi w\,\sigma_{v} = H(s/w)-(\sigma_{s}/\sigma_{v}w)\cdot H_{1}(s/w)$$
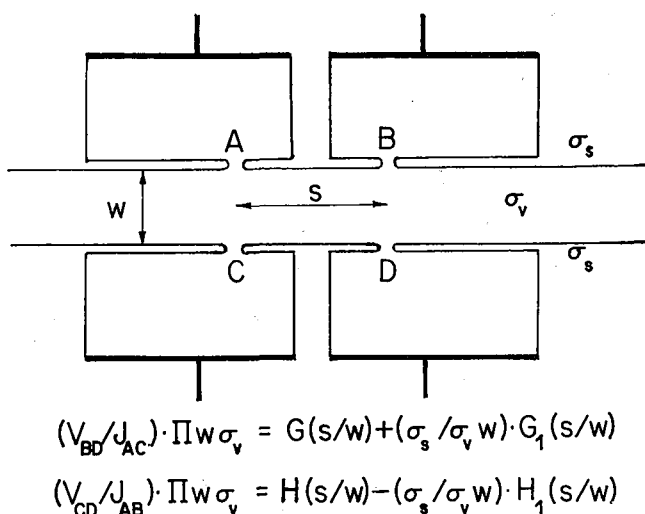
Fig. 1. Sample geometry in the four-point method (the functions G, H,
G$_1$ and H$_1$ are defined in the paper of Jaccard, 1966)

sample of thickness w with plane parallel faces has two probes on each side (A, B and
C, D) with a separation s. A current is injected first between A and C and the potential
is measured between B and D; then the current flows between A and B and the potential
is measured between C and D. The two resistance values obtained in this way are
related to the bulk and surface conductivities by functions of the ratio s/w which can
be computed easily. For practical reasons, the thickness and the probe separation were
chosen in the experiments at about 5 mm. To eliminate space charge effects, the elec-
trodes possessed a relatively large surface (for a low current density) and they were
mounted on ice blocks in a certain distance from the probe points. These consisted in
necks of 0.8 mm diameter which were produced by connecting the electrode blocks with
the sample through holes made in a thin plastic foil.

The samples were taken from high purity monocrystals, machined with a small lathe
and measured in a cold room at $-11°C$. The necks were doped in some cases with
hydrofluoric acid to improve their conductivity; the crystals were measured just after they
had been assembled (case a) and two days later (case b). As expected, the conductivities

Table 1. Volume conductivity σ_v and surface conductivity σ_s at $-11°C$
a) Pure ice; b) Pure ice doped with HF

	Cryst. No.	σ_v ohm^{-1} m^{-1}	σ_s ohm^{-1}	$W=\sigma_s/\sigma_v$ m
a)	1	6. 6×10^{-7}	1. 6×10^{-10}	2. 4×10^{-3}
	2	4. 5×10^{-8}	1. 4×10^{-10}	3. 1×10^{-3}
	3	6. 6×10^{-8}	1. 6×10^{-10}	2. 4×10^{-3}
	4	1. 9×10^{-7}	6. 3×10^{-10}	3. 4×10^{-3}
b)	1	4. 6×10^{-5}	8. 2×10^{-8}	1. 8×10^{-3}
	2	2. 9×10^{-5}	1. 0×10^{-7}	3. 6×10^{-3}

increased between the two measurements be-
cause of the acid diffusion. The results are
shown in Table 1.

To define the relative amount of surface
conduction, we have introduced the ratio W
of the two conductivities (which has the di-
mension of a length), which shows the same
order of magnitude of about 1 to 4 mm in all
the examined samples. It keeps this value
even when the ice is doped, as surface and
volume conductivities increase together.

Meander method. To test the above re-
sults, another measuring method has been
applied. The sample is machined from a
circular disc-shaped crystal in the form of a
meander-like prism (Fig. 2), the thickness w of
which is reduced after each measurement.
The total conductance (*i.e.* the inverse of the
resistance R) has a component proportional
to w, but the surface conductivity on the upper
and lower faces should contribute a constant
amount. This residual conductance by de-
creasing thickness is observed indeed, as it
can be seen by plotting the inverse resistance
vs. thickness (Fig. 3). The measured points
lie in a straight line which does not go through
the origin, but cuts the $1/R$-axis at a positive
value. The extrapolation of this line to the
left down to its intersection with the w-axis
yields then directly the characteristic length
W. All the examined crystals showed values
in the order of a millimeter for W, thus con-
firming the results obtained with the first
method. It was possible to mill certain sam-
ples down to a thickness of 0.3 mm, but a
kink never appeared in the $1/R$-diagramm.
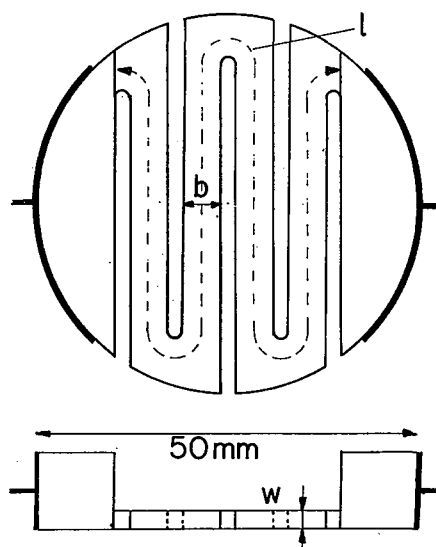
$$1/R = \sigma_v \cdot bw/l + \sigma_s \cdot 2(b+w)/l$$
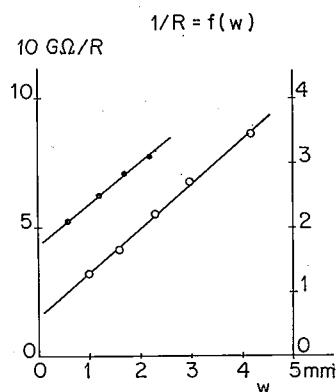
Fig. 2. Sample geometry in the meander
method

Fig. 3. Conductance of meander samples
as a function of their thickness
(pure ice at −11°C)

III. Effect of External Agents

Electric field. We tried to influence the surface conductivity of the meander samples
by applying a large static electric field perpendicular to the surface, and thereby to
eventually change the charge distribution in the surface layer. A Mylar foil with a
thickness of 0.011 mm was applied on the upper surface, with an aluminum foil on the
outer side as an electrode. Potentials up to 330 V were used, corresponding to fields of
at least $\pm 3 \times 10^6$ V/m, but no significant change in the conductivity could be observed.
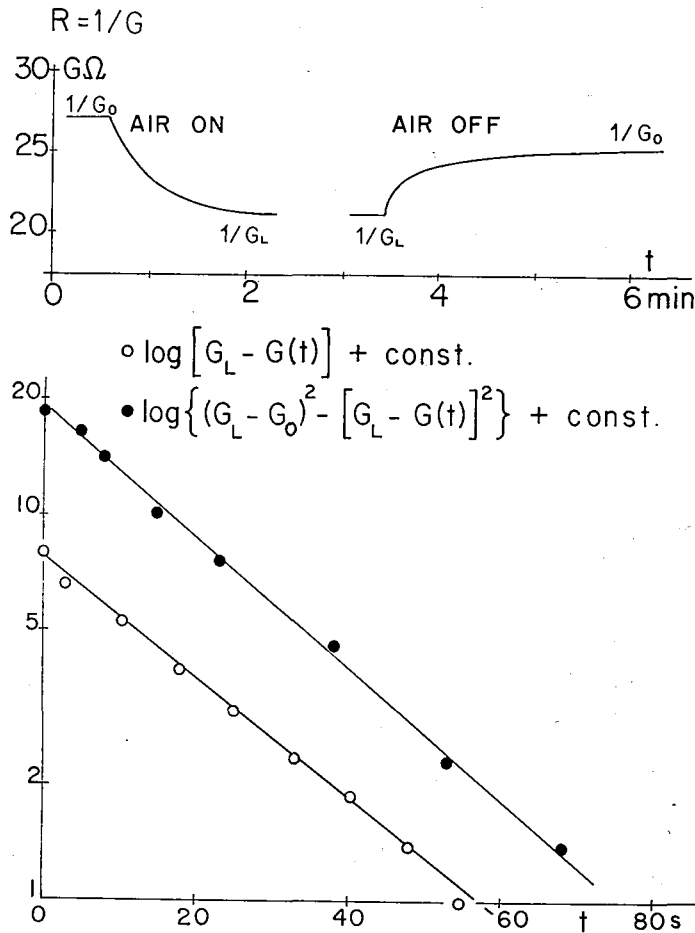
Fig. 4. Upper part: Behavior of the meander sample in an air current.
Lower part: Semilog plot of the conductance of the meander sample in the
air current as a function of time (transient behavior). Lower line, air stream
on; upper line, air stream off

Air current. While trying to cool a specimen in an air current from a small hair
dryer, we observed a strong variation of the resistance (up to 20%) when the current
was turned on and off. The air was passed through fine mesh wire nets, either earthed
or set at positive or negative potentials, but this did not affect the phenomenon. Thus
it is not likely to be a sort of electrostatic charging or discharging effect. As is seen
in Fig. 4, the air current reduces the resistance, but the transient process between the
two steady states is different if the current is turned on or if it is turned off. In the
first case, the resistance decrease begins with a rather small slope that corresponds to a
conductance change of the form e^{-t/t_1}. In the second case, this law is no longer valid
because the initial slope is too high and indicates rather a square root dependence of
the time. A good fit is achieved with the function $\sqrt{1-e^{-t/t_2}}$ as can be seen in the lower
diagramm of Fig. 4.

Air evacuation. The resistance has also been measured with the sample placed in a vacuum vessel. On evacuating, the process is more complex, with an initial high resistance peak followed by a slower increase. Filling the vessel with air brings a sharp decrease of the resistance down to a value lower than the initial one; the latter is reached again after about 30 seconds in the same way as in the air stream experiment.

IV. Discussion

The experiments described above indicate clearly the existence of a layer with a thickness of at most 0. 1 mm where the DC conductivity is at least one order of magnitude larger than in the bulk. The mobility and/or the concentration of the charge carriers must therefore be larger near the surface, but an interpretation is difficult without more experimental evidence.

The behavior of the transients cannot be explained by a simple thermal effect. When the air stream is turned on, the resistance decreases. This would require a temperature increase of the surface, but the temperature difference between the sample and the ambient air is much too small to account for the magnitude of the effect (20%). The sublimation is rather expected to play the predominant role, but it produces a decrease of the temperature, which should then be accompanied by an increase of the resistance, in contradiction with the observations. Moreover, a thermal effect would show a transient beginning with the square root of the time in both cases of the air being turned on and off.

The following hypothesis is a little more elaborate but offers a tentative plausible answer. The ice surface is normally occupied by a certain concentration n_{ss} of unknown species which are removed by the air stream according to the relations:

Air stream on: $n_{ss} = n_{sso}\, e^{-t/t_0}$,   (1)

Air stream off: $n_{ss} = n_{sso}\, [1 - e^{-t/t_0}]$.   (2)

They dissociate partially into traps, the concentration of which is proportional to the square root of n_{ss}. All these traps retain a certain number of the charge carriers, which are in the concentration n_c. The conductance varies then with n_c according to the expressions:

Air stream on: $\Delta(1/R) \propto \Delta n_c = -\Delta n_{co}\, e^{-t/2t_0}$,   (3)

Air stream off: $\Delta(1/R) \propto \Delta n_c = -\Delta n_{co}\, \sqrt{1 - e^{-t/t_0}}$.   (4)

The same occurs if the traps are directly removed by the air current and if the charge carriers are released from them according to a square root function.

A qualitative picture can be given without introducing other species than those present in the bulk. If the surface has really a structure with negative vertices pointing out, then the formation of a free surface on cutting through a crystal must be accompanied by a large outward flux of L defects in order to turn the right way the molecules which had before a positive vertex pointing away. This creates an electric field inside the crystal, which draws an excess of positive ions near the surface, where the D and OH^- are almost eliminated by recombination with the much more numerous L and H_3O^+. These associate with each other to form a sensitive amount of sessile pairs (L, H_3O^+),

postulated by Onager and Dupuis (1962), which do not contribute to the conductivity. When air is blown on, the surface layer sublimates and the L concentration drops to a lower value, liberating more ions, and returns to its equilibrium value when the air current is turned off, blocking again a part of the ions.

The time constant of the transient is governed by the diffusivity of the L, furnished from the bulk. A value of 10^{-10} m²/s obtained from a previous mobility estimation (Jaccard, 1959) indicates a thickness λ for the surface layer between 10^{-5} and 10^{-4} m, based on the observed transient time of about 20 s.

On the other hand, we have for the positive ions:

$$W = \sigma_s/\sigma_v = \lambda \sigma_+^*/\sigma_v = \lambda n_+^*/n_+ , \tag{5}$$

where the asterisks denote the quantities in the surface layer, and according to the Debye-Hückel theory:

$$\lambda^2 = \varepsilon\varepsilon_0 \cdot kT/n_+^* e^2 . \tag{6}$$

From these two expressions, the thickness λ and the concentration $\bar{n}_+^*$ can be calculated. With $W = 2 \times 10^{-3}$ m, $n_+ = 10^{16}$ m⁻³, $\varepsilon\varepsilon_0 = 10^{-9}$ A·s/V·m, $kT/e = 2 \times 10^{-2}$ V and $e = 10^{-19}$ A·s, we obtain a thickness λ of about 10^{-5} m which agrees with the estimated diffusion length. The H_3O^+ concentration near the surface n_+^* is then about 10^{18} m⁻³, only two orders of magnitude higher than in the bulk.

V. Conclusion

Unlike other phenomena which can be explained without any special hypothesis for the surface structure, the experiments described here oblige to assume that the ice surface layers differ markedly from the bulk as far as the electrical conductivity is concerned, and must consequently differ also in their structure. The microscopical interpretation given in section IV has the advantage of being simple and to make use of well known defects of the bulk only, but it must be considered as tentative, until more experimental evidence becomes available.

The interpretation is based on Fletcher's picture of the liquid-like surface layer; according to Fletcher, it should have a thickness of about 40 Å at the considered temperature. Our estimation yields a much higher value of about 10^{-5} m but this is not a contradiction: the electrically active layer need not to be identical with the disordered one. This view is supported by a consideration of the order of magnitude for the conductivity in the liquid-like layer. Because of the disorder the ionic mobility is determined there by the molecular reorientation and is therefore much lower than the bulk, attaining at most the value it has in water. With a layer thickness of 40 Å, the local conductivity must be there at least of the order of 10^{-2} $\Omega^{-1} \cdot$m⁻¹. This requires a high concentration of charge carriers, (e.g. more hydroxonium ions than are produced in water by hydrofluoric acid in a concentration of 10^{-4}) and it is difficult to see which chemical agent could produce these charge carriers, and which mechanism would account for the transient behavior in the air stream. On the other hand, the explanation of section IV seems to yield reasonable values; therefore, the liquid-like layer hypothesis is not infirmed by these experiments, but must rather be indirectly postulated.

In any case, it would be premature to attribute too much signification to any detailed theory now ; the experiments have been performed only under primitive conditions, and better and extensive measurements are necessary to solve the problems mentioned here.

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