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CORRESPONDENCE

The Editor,

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SIR,

*On electric polarization in ice**

In a recent article by Østrem (1967), attention is drawn to polarization effects observed in D.C. resistivity measurements on ice. In this connection, some earlier studies by Workman, Truby and the present author deserve mentioning. Together with Workman, Truby (1953) observed remarkably pronounced polarization effects in D.C. measurements of the resistivity of both pure ice and ice frozen from various dilute solutions (such as 10^{-6} molar cesium fluoride and ammonia). The polarization was manifested as highly unexpected results in the D.C. measurements of the ice resistivity. Thus, the apparent resistance of the ice samples was initially found to depend on the direction of the applied potential, compared to the direction in which the ice had originally grown. Apparent "rectification ratios" of about 30 000 were commonly observed. The crystals used in these studies were slowly grown at rates of a few (up to twenty) micrometers per second; often under very closely controlled conditions. The samples appeared by petrographic microscope examination and by standard X-ray diffraction techniques to be single crystals. The crystals were perfectly clear and free of bubbles, but did, in fact, possess a microstructure (Workman, 1953; Truby, 1955). The direction of highest resistance corresponded to a flow of protons toward the surface from which the ice grew, the rectification phenomenon described being extremely sensitive to the nature and amount of impurities in the solution frozen. In a study by Workman and others (unpublished), it was observed that at $-21°C$, the conductivity of a fresh sample of ice, frozen from a 10^{-6} molar cesium fluoride solution is about $2 \times 10^{-9}\ \Omega^{-1}\ cm^{-1}$. However, the apparent conductivity of the ice depended on the potential difference across the sample. Figure 1 shows in a somewhat schematic fashion, the conductance versus field strength. This curve shows a distinct hysteresis loop, although attempts were made to minimize transient effects by allowing the current in each measurement to pass through the sample for about twenty minutes. It was found that this procedure resulted in some semblance of steady-state behavior. As can be seen from the graph, in the case described a 60 000-fold change in resistance was observed, while in other cases, "rectification ratios" of 10^{+5} were observed. The resistance of "pure ice" was less sensitive to variations in field strength, by three to four orders of magnitude, than the resistance of ice frozen from dilute solutions containing cesium fluoride. It might be mentioned in passing that fields of 60 000 V cm^{-1} could be applied without breakdown. Furthermore, the observed rectifying properties appeared to vanish at low frequencies, being approximately half at 60 Hz and almost completely eliminated at 200 Hz.

At the time of the original measurements, it was thought that the rectification observed was associated with the microstructure of ice (Truby, 1955; Gentile and Drost-Hansen, 1956; see also Drost-Hansen, 1967) and an electronic conduction mechanism. Subsequent study (Workman and others, 1954) demonstrated that the conduction was entirely protonic (or, at least, that the discharge phenomena at the ice–metal interfaces was protonic). When it was recognized that the conduction was by protons rather than electronic, the question of electrode polarization was re-examined and the previously suspected "bulk rectification" proved not to be real. In this connection, it should be noted that many measurements were made with four-electrode configurations. It is speculated that even with the probe electrodes used in the four-electrode configuration, electrodepolarization effects may occur in the measurements. Electrometers and electrostatic voltmeters with very high input impedances ($10^{+14}\ \Omega$ or higher) were used, but even so, a certain amount of polarization will occur due to the displacement current necessary to bring the wires and the electrometer up to the observed potential. Workman and Truby (unpublished) and further studies by Carlin (unpublished), working with the present author, have shown that a pre-treatment of the platinum disk electrodes, commonly used in these ice studies, may play a dominant role in determining the interfacial resistive properties. Thus, by electrolysis in dilute solutions, prior to freezing the electrodes onto the ice sample, it was possible to change the "sense of direction" of the rectification phenomenon by either depositing a layer of hydrogen or a layer of oxygen on the electrodes. Thus, the rectification was made to depend on the electrolytic pretreatment rather than the direction of growth of the ice. Similar results were also found by Carlin using gold, copper, nickel, aluminum and carbon electrodes.

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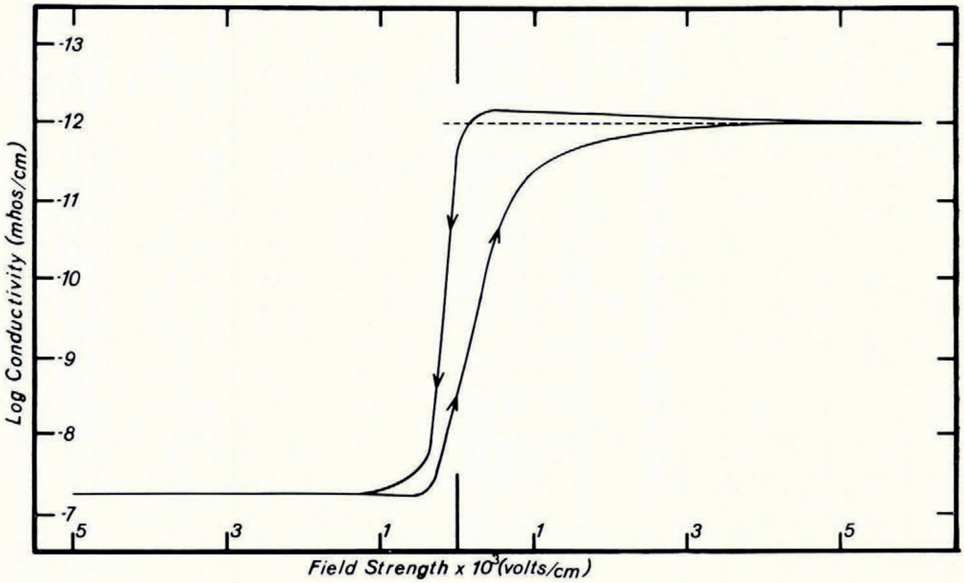

Fig. 1. Conductivity versus applied field strength for ice frozen from 10^{-6} molar cesium fluoride solution. Positive values of field strength correspond to flow of protons toward original ice–metal interface from which the ice was frozen.

In summary, the author wishes to point to the dangers of electrode polarization phenomena in all d.c. measurements on ice (whether in naturally occurring ice or ice frozen in the laboratory) and the subsequent difficulties in ascribing unequivocally any observed, anomalous behavior to the structure and properties of the bulk ice. At the same time, a real effect may possibly exist due to partial charge accumulation effects at the interfaces between the microstructural units in the ice. Since the microstructure can be eliminated by increasing the electrolyte concentration, it is expected that the polarization effects may diminish or disappear at relatively low concentrations of electrolyte, say 10^{-3} or 10^{-4} molar. In general, d.c. conductivity is probably of limited use only for characterizing ice samples and a.c. measurements are generally to be preferred. Camp and others (1967) have recently published a careful study of the electrical conduction in ice which may serve as a model for experimental studies of conductivity in protonic semi-conduction. See also the recent review article by Gross (1968).

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SIR, *Reply to Mr J. G. Paren's comments on "Dielectric relaxation in temperate glaciers"*

Paren (1968) has formulated the theory for my capacitance measurements made with two wires laid on a glacier surface (Gribbon, 1967). He pointed out the difficulties in sampling the ice properties deep inside the glacier in the presence of high d.c. conductivity, and concluded that the wires tended to provide information on the snow close to their surface and could not detect any discontinuity within the glacier readily.

His conclusions are confirmed by further measurements made by W. T. Band, D. T. Meldrum, R. M. Nisbet and myself during the 1967 University of St Andrews expedition to Upernivik Ø (lat. 71° N., long. 52° W.) when we found that our fixed buried wire systems of separation $b = 0.2$ m and $b = 20$ m placed just below the surface of a soaked facies *névé* layer overlying glacial ice to a depth of 1.5 m gave identical results. If the wide wires had sampled below the *névé*–ice discontinuity, the apparent relaxation frequency f_m would be different from that for the close wires but no difference was detected between the time-averaged apparent relaxation frequencies of the two wire systems.

For comparison we also used a parallel plate capacitor imbedded at different depths in the layer and found similar f_m values to those measured with the wires. In this simple geometry we found that both f_m and f_r (the relaxation frequency defined for a conductivity equal to the mean of the static and high frequency conductivities) depended on the depth of the capacitor, with a minimum f_r value occurring at a region of high conductivity snow at its melting point. Higher ϵ' and ϵ'' values were found with wet snow than with the same sample frozen, indicating that surface conduction rather than bulk conduction effects influenced the wet snow results markedly. However, the wire measurements were insensitive to these localized effects and could not detect any depth variations so lending further support to Paren's conclusions on the validity of the wire measurements.

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