

THE ELECTRICAL PROPERTIES OF ICE SURFACES

By NORIKAZU MAENO and HIROSHI NISHIMURA

Institute of Low Temperature Science, Hokkaido University, Sapporo, Japan 060)

ABSTRACT. The surface conductivity of monocrystalline ice was measured as a function of temperature, impurity concentration, field-strength, and other variables. At temperatures below about -6°C the surface conductivity was found to follow the Arrhenius equation with an activation energy of 33 ± 2 kcal mol $^{-1}$ (1.43 ± 0.09 eV). Small amounts of impurities contained within the ice increased the surface conductivity and decreased the activation energy: for HF-doped ice the activation energy was reduced to 10.0 kcal mol $^{-1}$ (0.44 eV). Mechanical treatment of the ice surface increased the surface conduction. At temperatures above about -6°C the surface conductivity increased more rapidly with the rise in temperature; this is explained in terms of the appearance and development of a quasi-liquid layer on the ice surface. The electrical behaviour of sublimed ice surfaces was found to vary at a temperature around -9°C . At higher temperatures a sharp, instantaneous current increase was observed as evacuation began; this was considered to be caused by the formation of ionic states due to the rapid evaporation of quasi-liquid layers. It was concluded that the temperature above which the ice surface was covered with a quasi-liquid layer lay in the range -6 to -9°C .

RÉSUMÉ. Propriétés électriques de la surface de la glace. La conductivité superficielle de la glace monocristalline a été mesurée en fonction de la température, de la concentration en impuretés, de l'intensité du champ appliqué, ... etc. A des températures inférieures à -6°C , nous avons observé que cette conductivité suit une loi d'Arrhenius avec une énergie d'activation de 33 ± 2 kcal mol $^{-1}$ ($1,43 \pm 0,09$ eV). Une teneur faible en impuretés dans la glace entraîne une augmentation de la conductivité superficielle et une diminution de l'énergie d'activation: dans le cas de la glace dopée avec HF, l'énergie d'activation est abaissée de 10,0 kcal mol $^{-1}$ (0,44 eV). Des traitements mécaniques de la surface de la glace accroissent également la conductivité superficielle. Au-dessus de -6°C , la conductivité superficielle croît plus rapidement avec la température et nous avons attribué ce fait à l'apparition et au développement d'une couche quasi-liquide sur la surface de la glace. Le comportement électrique de surfaces de glace en cours de sublimation présente une variation aux environs de -9°C : aux températures plus élevées, nous observons une augmentation pratiquement instantanée du courant dès que s'amorce la sublimation et nous avons considéré que cela est dû à la formation d'ions résultant de l'évaporation rapide de la couche quasi-liquide. Nous en avons conclu que la température critique au-dessus de laquelle la surface et la glace se recouvre d'une couche quasi liquide se situe entre -6 et -9°C .

ZUSAMMENFASSUNG. Die elektrischen Eigenschaften von Eisoberflächen. Die Oberflächenleitfähigkeit von einkristallinem Eis wurde in Abhängigkeit der Temperatur, der Verunreinigungskonzentration, der Feldstärke und anderer Größen gemessen. Es wurde gefunden, dass sie bei Temperaturen unterhalb -6°C der Arrhenius-Gleichung gehorcht, mit einer Aktivierungsenergie von 33 ± 2 kcal mol $^{-1}$ ($1,43 \pm 0,09$ eV). Geringe Verunreinigungen im Eis erhöhten die Oberflächenleitfähigkeit und erniedrigten die Aktivierungsenergie: bei HF-dotiertem Eis wurde die Aktivierungsenergie auf 10,0 kcal mol $^{-1}$ (0,44 eV) herabgesetzt. Mechanische Bearbeitung der Eisoberfläche vergrößerte die Oberflächenleitung. Bei Temperaturen oberhalb -6°C wuchs die Oberflächenleitfähigkeit mit steigender Temperatur schneller. Dies wurde mit dem Auftreten und der Ausbildung einer quasi-flüssigen Oberflächenschicht auf dem Eis erklärt. Es wurde festgestellt, dass das elektrische Verhalten abdampfender Eisoberflächen sich bei einer Temperatur von rund -9°C ändert: bei höheren Temperaturen wurde mit Beginn des Abpumpens ein scharfer, unverzüglicher Anstieg beobachtet. Als Ursache dafür wurde die Bildung von Ionenzuständen durch die rasche Verdampfung der quasi-flüssigen Schicht angesehen. Es wurde gefolgert, dass die kritische Temperatur, oberhalb derer die Oberfläche mit einer quasi-flüssigen Schicht bedeckt war, zwischen -6 und -9°C lag.

1. INTRODUCTION

The physical properties of ice surfaces have been the subject of much study by ice researchers ever since the work of Faraday in 1860. The large amount of theoretical and experimental investigations in this field are reviewed by Jellinek (1967), who paid particular attention to the possibility of the existence of a quasi-liquid transition layer on the surface of ice crystals in equilibrium at temperatures below the melting point. However, essential problems remain unsolved mainly because the subject has been often treated only as an incidental phenomenon which appears during measurements of other bulk properties of ice. Few experiments have concentrated on the specific surface properties of ice by a systematic exclusion of these bulk properties. Mason and others (1963) found that the mean surface diffusion length of water molecules increased rapidly as the temperature approached the melting point of ice; Bullemer and Riehl (1966) separated the surface conduction from the

bulk conduction to obtain an activation energy for the surface effect of 30 kcal mol^{-1} (1.30 eV). Jaccard (1967) found the surface conductivity to be of the order of $10^{-10} \Omega^{-1}$ at -11°C . Maeno (1973[a]) measured the surface conductivity of a flat surface of monocrystalline ice as a function of temperature and found that the mechanism of surface conduction changed at a temperature around -6°C suggesting the occurrence of a surface phase change at this temperature. Kvlivdze and others (1974) performed proton magnetic resonance studies on finely divided ice and found evidence that a mobile phase developed on the ice surface above -10°C .

In the present study the electrical properties of ice surfaces were investigated in more detail than previously (Maeno, 1973[a]). The electrical surface conduction of monocrystalline ice was measured as a function of temperature, crystallographic orientation, impurity concentration, field strength, and other external conditions such as mechanical treatment and sublimation. The study was designed to investigate the detailed dependence of surface conductivity upon the temperature and purity, and it was hoped to obtain more information about the electrical properties of ice surfaces.

2. APPARATUS AND EXPERIMENTS

The surface conductivity of monocrystalline ice was measured by using three chromium-plated copper electrodes, which are designated A, B, and C in Figure 1. The radii of the circular electrodes A and C were 6.0 and 25.0 mm respectively. B was ring-shaped with an inner radius of 11.0 mm, so that the distance between A and B on the test surface of an ice specimen was 5.0 mm. The thickness of an ice sample was smaller than half the distance between the electrodes A and B to eliminate bulk conduction from the surface measurement. When an electric potential was applied between A and B, an instantaneous surface current was observed which decreased with time. Surface conductivities were calculated from the surface conductance when a steady state had been attained, usually one minute after the application of a potential difference. The d.c. power supply was provided by Takasago GP050-2, Toa SV1-A, and Metronix 665B instruments, and the current measurements were made using an electronic picoammeter (Takeda TR-8641).

The electrode system was set in an O-ring-sealed chamber of dimension $0.115 \times 0.100 \times 0.100 \text{ m}^3$ which was made of brass 6.0 mm thick, and the chamber was immersed in a liquid-filled thermostat, the temperature of which was maintained between 0 and -30°C with an accuracy of $\pm 0.05^\circ\text{C}$.

Three kinds of monocrystalline ice were used as specimens in the experiments:

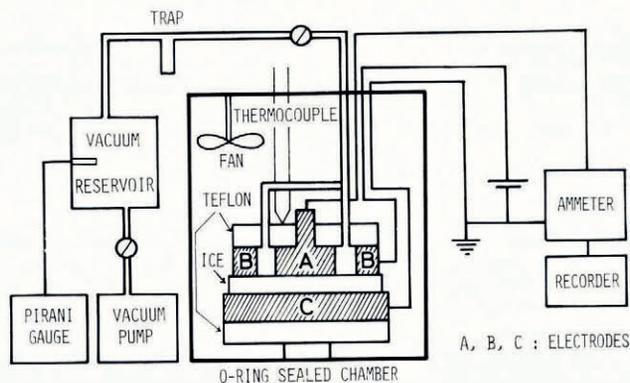


Fig. 1. The experimental apparatus.

- (1) Pure artificial ice, which was grown from ion-exchanged distilled water (electrical conductivity of $10^{-4} \Omega^{-1} \text{m}^{-1}$ at 25°C) in an apparatus already described in Maeno (1973[b]).
- (2) "Pure" natural ice, which was collected at "O-ike" pond near the "Syowa" station in Antarctica. The ice was formed from naturally frozen water supplied from precipitation and snow drifts, and was composed of monocrystalline grains roughly 0.1 m in diameter. Though the conductivity of its melt was as low as $(3-4) \times 10^{-4} \Omega^{-1} \text{m}^{-1}$ and was considered to be almost pure, some impurity effects were noted in the experiments as discussed below.
- (3) HF-doped ice, which was grown from an HF aqueous solution in a similar way to (1). The fluorine concentration in the ice was determined with a specific-ion electrode (Corning-Yanagimoto) after the electrical measurements were finished.

Ice specimens were prepared by planing with a fine blade and then polishing with fine emery paper and a gauze until their thickness was less than half the distance between the electrodes A and B (about 2 mm). This was necessary to exclude the effects of bulk conduction from the measurements of surface conduction. The crystallographic orientation of the test surface was determined by the evaporation etch-pit method. Most of the measurements were carried out on basal (0001) planes. Ice specimens were fixed to the electrodes by a minimal amount of thawing and refreezing.

The electrical properties of subliming ice surfaces were studied by evacuating the air above the ice surface with a vacuum pump. The total pressure was measured with a Pirani gauge and automatically recorded (Fig. 1). Measurements were carried out at a pressure of 15 mm Hg (0.113 Pa), in most cases. The surface temperatures and the temperatures within the subliming ice specimens were measured separately using 0.1 mm copper-constantan thermocouples. The accuracy of the temperature measurements was ± 0.05 deg.

3. EXPERIMENTAL RESULTS

(a) Surface conductivity

Figure 2 shows the relationship between the surface conductivity and the reciprocal of the absolute temperature for the different types of monocrystalline ice. Results for the pure artificial ice are shown as a hatched region: slight changes in the surface preparation causes small increases in the measured values although the temperature dependence of each sample is similar. The temperature dependence for the pure monocrystalline ice follows the Arrhenius equation below about -6°C and its activation energy was $33 \pm 2 \text{ kcal mol}^{-1}$ ($1.43 \pm 0.09 \text{ eV}$). The boundaries of the hatched region coincide with the maximum and minimum values for natural monocrystalline ice collected from the Mendenhall Glacier in Alaska (Maeno, 1973[a]).

Surface conductivities of "pure" natural (O-ike) ice are slightly larger than those of the pure artificial and Mendenhall Glacier ices, but their temperature dependences are similar: the activation energy below about -6°C ranged from $25.5 \text{ kcal mol}^{-1}$ (1.11 eV) to $33.1 \text{ kcal mol}^{-1}$ (1.43 eV), the average being $27.3 \text{ kcal mol}^{-1}$ (1.19 eV). The deviations from the pure ice are considered to be caused by the possible incorporation of slight amounts of impurities during natural freezing.

General features for these three kinds of pure monocrystalline ice are that, at temperatures below about -6°C the surface conductivity follows the Arrhenius equation, but that at temperatures above -6°C it increases more rapidly as the temperature is raised, which suggests the important roles of the quasi-liquid layer in the surface conduction near the melting point of ice.

The surface conductivities of HF-doped ice are larger by two orders of magnitude than those of pure ice whereas the activation energies are smaller, i.e. $10.0 \text{ kcal mol}^{-1}$ (0.44 eV) on average. Some of the results are shown in Figure 2 for HF-doped ices of concentrations $4.8 \times 10^{-5} \text{ M}$, $7.5 \times 10^{-5} \text{ M}$, and $1.7 \times 10^{-4} \text{ M}$, where M denotes mol kg^{-1} . Furthermore, rapid changes near the melting point were not observed.

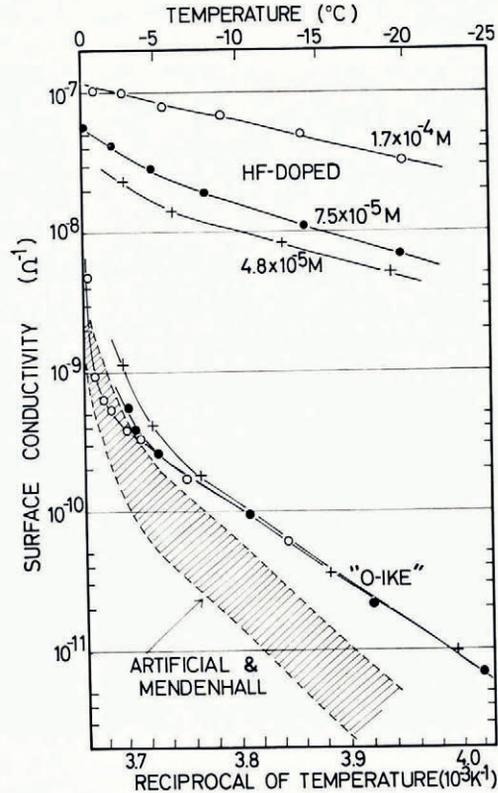


Fig. 2. Surface conductivity versus the reciprocal of the absolute temperature for (0001) planes of various kinds of ice.

(b) *Effects of mechanical treatment*

The effects of mechanical treatments on the surface conductance were investigated. In these experiments, larger electrodes were used: the radius of the central electrode was 25.0 mm and the inner radius of the ring-shaped electrode was 35.0 mm. The ice surface was polished with an emery paper of grit number 320 and then a p.d. of 10.00 V (at -16.0°C) was applied to the ice so that a steady current was passed through the surface. Figure 3 is a photomicrograph of the polished surface. Calculations indicate that the macroscopic surface area has increased by 20%, thus the electric current should decrease by the same amount. However, the current increased by 44%, which implies that the mechanical polishing has increased the number of electrically active ions and the thickness of the conduction layer on the ice surface. When the ice specimen was kept at -16.0°C for five days, the mechanical disturbances relaxed and the current fell until it was 16% greater than the original value before polishing.

An increase in the surface conduction was observed even when the ice surface was scratched with a fine needle, although the increase was only a few per cent.

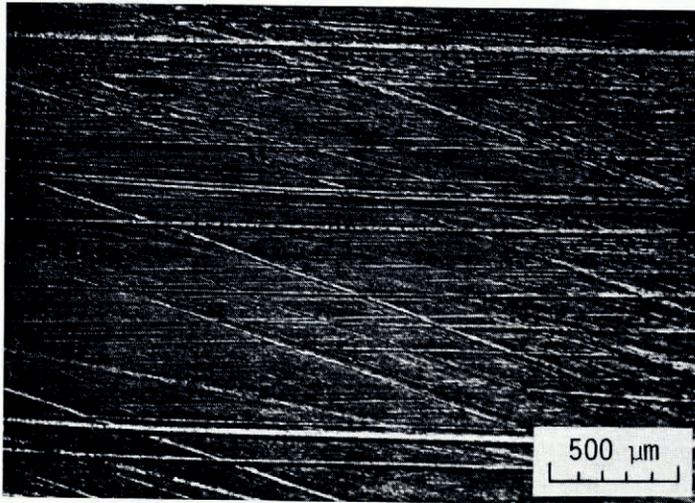


Fig. 3. Photomicrograph showing the ice surface treated with an emery paper.

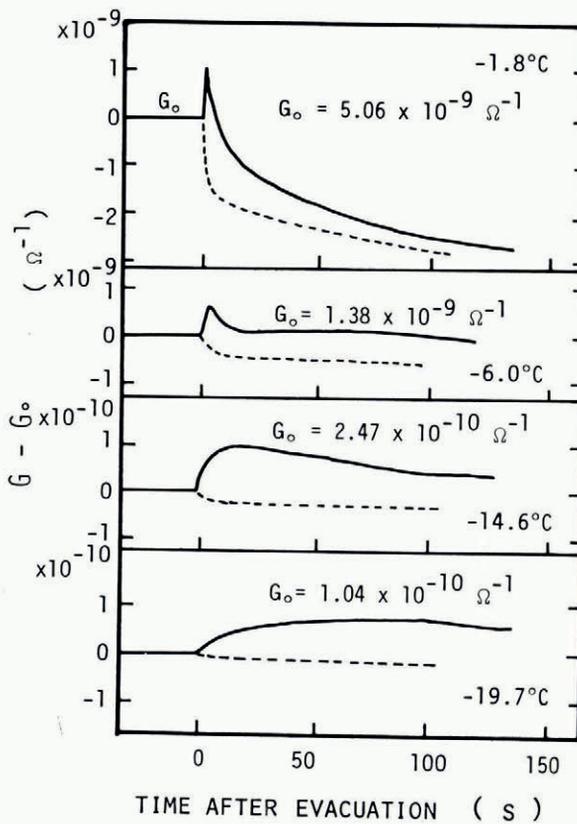


Fig. 4. Variations of surface conductance after evacuation for "pure" natural ice ("O-ike"). A potential of 5.00 V is applied with a steady conductance of G_0 . Dashed lines indicate expected variations of conductance calculated from measured temperature of ice surface using the results of Figure 2.

(c) *Effects of sublimation*

It has been reported that surface conduction increases if the ice surface is maintained under a reduced pressure (Jaccard, 1967; Maeno, 1973[a]), but the results of the two authors were different. Figure 4 shows variations in the surface conductance after the evacuation of air above the surface of "pure" natural ice. G_0 is the surface conductance at atmospheric pressure.

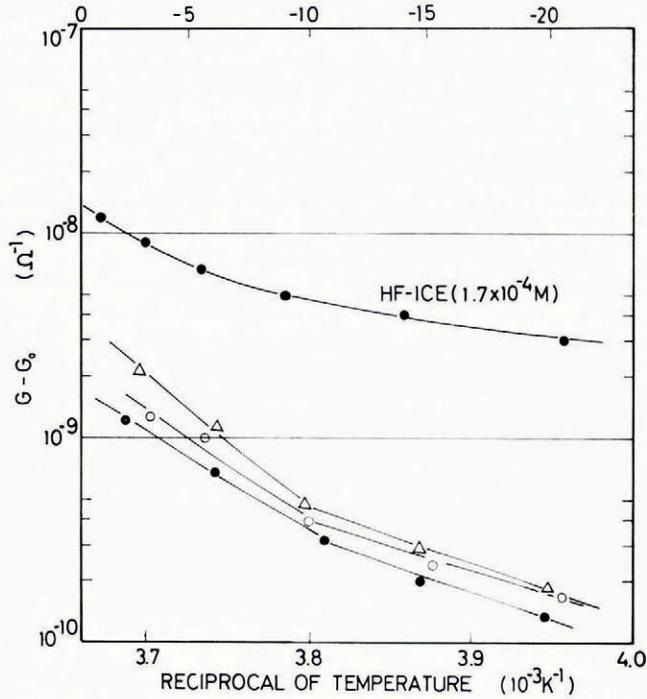


Fig. 5. Maximum variations of surface conductance versus the reciprocal of temperature for "pure" natural and HF-doped ($1.7 \times 10^{-4} M$) ice.

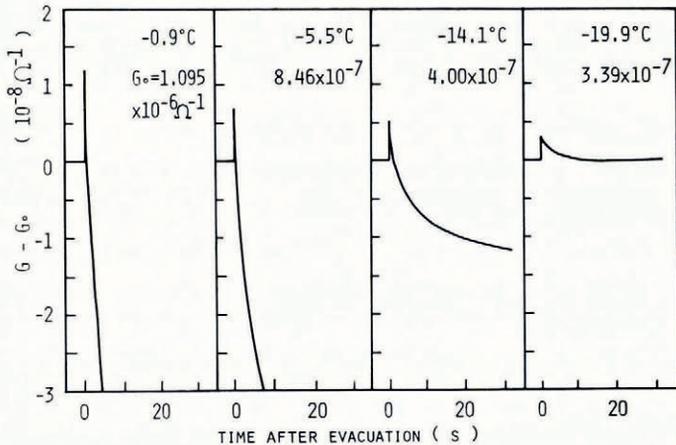


Fig. 6. Variations of surface conductance after evacuation for HF-doped ice ($1.7 \times 10^{-4} M$). 10.00 V is applied with a steady conductance of G_0 .

The behaviour was found to change at a temperature close to -9°C . At higher temperatures the surface conductance increased instantaneously and then decreased gradually. On the other hand, at lower temperatures it did not show the initial sharp increase but rose slowly, and then decreased more slowly. Maximum values of the change in the surface conductance were plotted against the reciprocal of the temperature (Fig. 5). It is noted that the temperature dependence changes at a critical temperature of about -9°C .

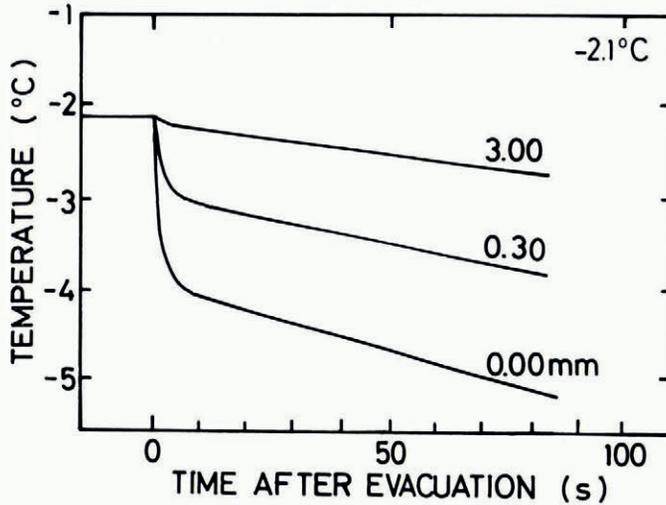


Fig. 7. Variations of temperature of subliming ice for 0.00, 0.30, and 3.00 mm from the surface.

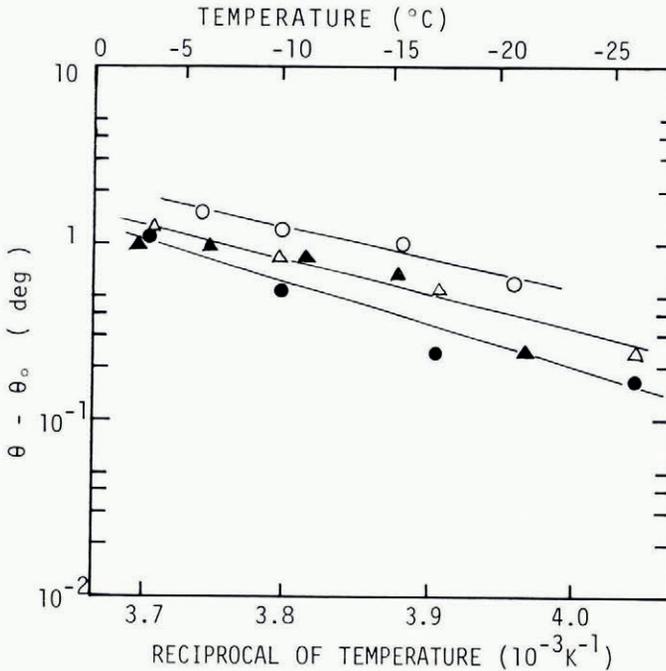


Fig. 8. Decrease of surface temperature versus the reciprocal of temperature.

The effects of sublimation were also investigated using HF-doped ice. Figure 6 shows some examples of surface-conductance variations, after evacuation, for a specimen containing 1.7×10^{-4} M of fluorine. Its behaviour was almost the same as that of pure ice at temperatures above -9°C , though the magnitudes were an order of magnitude larger than those of pure ice (Fig. 5).

Figure 7 shows the change in temperature of "pure" ice after the evacuation had begun. Rapid changes occur within 10 s, and then the decrease of temperature becomes slower and almost steady as an equilibrium is set up with bulk thermal conduction. The decrease of the surface temperature 10 s after the evacuation was plotted against the reciprocal of temperature in Figure 8.

(d) *Field-strength dependence*

Most of the measurements quoted above were conducted on ice surfaces in which the electric fields were about 0.20 V m^{-1} . Measurements were made at higher fields in order to find any saturation phenomena of current or charge in the surface conduction, as has been reported for bulk conduction by Eigen and others (1964), and Maidique and others (1971). However, with the electric fields studied in this part of the present investigation ($\approx 300 \text{ kV m}^{-1}$) the surface currents were proportional to the applied field strength and no saturation effects were found.

4. DISCUSSION

Below a critical temperature of about -6°C , the surface conductivity of (0001) planes of pure ice crystals was represented fairly well by an Arrhenius equation with an activation energy of $33 \pm 2 \text{ kcal mol}^{-1}$ ($1.43 \pm 0.09 \text{ eV}$). Small amounts of impurity caused an increase in the surface conductivity and a decrease in the activation energy: for HF-doped ice the activation energy was reduced to $10.0 \text{ kcal mol}^{-1}$ (0.44 eV). If it is assumed that, just as for the bulk conduction in pure ice, the surface conductivity is determined only by the concentration and mobility of charge carriers, presumably hydroxonium (H_3O^+) ions, the observed activation energy gives the sum of the formation and translation energies of the ions in the surface region. Since the activation energy for d.c. bulk conduction in pure ice is reported to range from $8.0 \text{ kcal mol}^{-1}$ (0.35 eV ; Bullemer and others, 1969) to $14.0 \text{ kcal mol}^{-1}$ (0.61 eV ; Jaccard, 1959), the experimental result here suggests that the ions in the surface region are two to four times more difficult to form and move than bulk ions, and that doping, especially by fluorine impurities, makes their formation and movement easier. This is also supported by the observation that the mechanical disturbance of an ice surface increases the surface conduction since it produces many lattice defects and electrically-mobile ion states in the surface region. An alternative explanation for the high activation energy is that the measured energy includes other temperature dependences, e.g. relaxation time for the replacement of surface molecules, drift distance of charge carriers, etc., but we have no evidence to check which is the true mechanism.

The experimental observation that the dependence of surface conductivity on temperature changed at about -6°C , and that it increased more rapidly as the temperature approached the melting point gives strong evidence for the appearance and development of a quasi-liquid layer on the ice surface, because molecules in such a layer are more mobile and electrically active defects are more abundant. According to the semi-quantitative theory of Fletcher (1968), the surface of ice is covered with a quasi-liquid layer at temperatures above about $(-5 \pm 3)^\circ\text{C}$ and the density of ions in the layer may be estimated as $3.3 \times 10^{17} \text{ m}^{-2}$ at 0°C (Fletcher, 1968, fig. 1). Then, the surface conductivity is computed as roughly $1.1 \times 10^{-8} \Omega^{-1}$ assuming the mobility to be that of liquid water, namely $2.1 \times 10^{-7} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$, which agrees well with our experimental result.

The time dependence of surface conduction in pure ice undergoing sublimation changed at a temperature around -9°C . The instantaneous, sharp increase in surface conductance when evacuation began was only observed at higher temperatures with pure ice, but HF-doped ice showed an initial increase at all temperatures studied in the present investigation. We consider that these increases in conductance are related to the presence of quasi-liquid layers on the ice surface. They cannot be explained as thermal effects, the dashed lines in Figure 4 represent expected changes of surface conductance calculated from the measured temperature of the ice surface using the results of Figure 2.

At higher temperatures the instantaneous evaporation of the quasi-liquid layer should produce a strongly strained region on the surface which should in turn form momentary lattice defects (especially ionic and orientational defects), because the value of the sublimation coefficient is probably higher than that of solid ice. This strain causes the initial sharp increase in surface conductance, which increase is then followed by a decrease due to the cooling by sublimation. At lower temperatures, such a sudden increase of conductance does not occur since either no quasi-liquid layers exist on the ice surfaces or, if they do exist, their effects are negligibly small so that the sublimation is not strong enough to form electrically active defects instantaneously. Nevertheless, the surface conductance gradually increases to saturation in about 10 s. It seems that the disagreement between the observations of Jaccard (1967) and Maeno (1973[a]) might be due to the temperature differences between measurements. Jaccard observed the behaviour of subliming ice at lower temperatures, and Maeno at higher temperatures.

The decrease in surface conductance following the initial increase is a result of surface cooling due to sublimation; the effect is greater at warmer temperatures and, if any impurities are incorporated in the specimen, at higher concentrations. The rate of sublimation was calculated from the temperature of the ice surface by assuming that surface molecules are removed at a constant rate and that the heat flux across the surface is constant. The rate of sublimation \mathcal{J} (using the theory of heat conduction (Carslaw and Jaeger, 1959)) is written as

$$\mathcal{J} = \frac{K(\theta - \theta_0)}{2L} \left(\frac{\pi}{\alpha t} \right)^{\frac{1}{2}}, \quad (1)$$

where α and K are respectively the thermal diffusivity and conductivity of ice, L is the latent heat of sublimation of ice, $(\theta - \theta_0)$ is the change of the surface temperature after the evacuation, and t is the time. Figure 9 shows the results computed from Equation (1) using temperatures at 10 s after the initiation of evacuation. In the computations, the values of α , K , and L were assumed not to change in the temperature range in question. It is seen in Figure 9 that values of \mathcal{J} are smaller by three orders of magnitude than the theoretical maximum rate of sublimation \mathcal{J}_{\max} , which can be estimated from the equilibrium vapour pressure P_{eq} of ice as

$$\mathcal{J}_{\max} = P_{\text{eq}}(2\pi MRT)^{-\frac{1}{2}} \approx \mathcal{J}_0 \exp\left(-\frac{H_{\text{eq}}}{RT}\right), \quad (2)$$

here M is the molecular weight of water, R the gas constant, T the absolute temperature, \mathcal{J}_0 a constant, and H_{eq} the equilibrium enthalpy of sublimation, which has the value $12.2 \text{ kcal mol}^{-1}$ (0.530 eV). The deviation of the obtained values of \mathcal{J} from \mathcal{J}_{\max} might be partly because the vacuum was not low enough and partly because the sublimation coefficient of ice is small (Delaney and others, 1964). The activation enthalpy of sublimation H was estimated as $8.3 \text{ kcal mol}^{-1}$ (0.361 eV) from the straight lines in Figure 9. Although the value is rather larger than one-half of H_{eq} it suggests that the rate-determining process in the sublimation of ice in our temperature range is that of the formation of one-hydrogen-bonded molecules, which can be accomplished by breaking one hydrogen bond of a two-bonded molecule in the surface region of ice crystals, as proposed by Davy and Samorjai (1971).

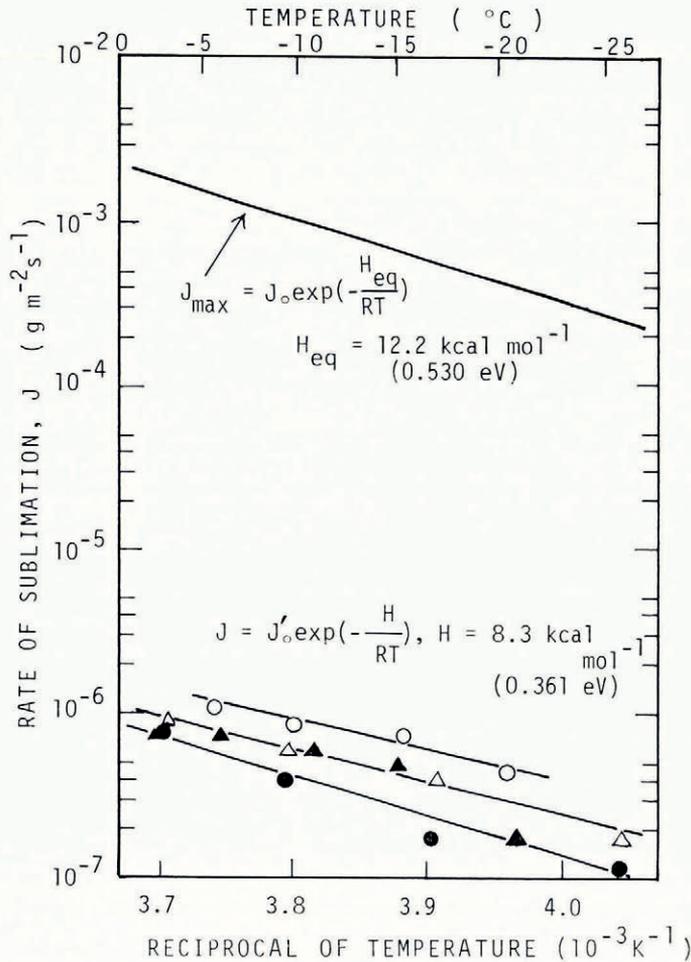


Fig. 9. Rate of sublimation versus the reciprocal of temperature.

In obtaining the rate of sublimation and activation enthalpy we have used the same values at all temperatures for α , K , and L , but this is not precisely correct; we must use a smaller value of L when the ice is covered with a quasi-liquid layer. Then, if we know correct values for the constants relating to the quasi-liquid layer and apply them to Equation (1), \bar{J} and H would become larger than shown in Figure 9 at temperatures at which quasi-liquid layers exist, and a kink would appear in the curve of \bar{J} at a temperature around -9°C in accordance with the temperature dependence of surface conductance.

The reason that the electrical behaviour of ice under vacuum changed at a temperature about 3 deg lower than that at which the surface conductivity began to increase more rapidly, may be that the transient properties under vacuum are more sensitive to the presence of quasi-liquid layers on the ice surfaces. Therefore, it is concluded from our results of electrical measurements that the critical temperature above which the ice surface is covered with a stable quasi-liquid layer is between -6 and -9°C .

ACKNOWLEDGEMENT

The authors are indebted to Hideki Narita of Hokkaido University for providing them with the specimens of ice which were collected at "O-ike" in Antarctica.

REFERENCES

- Bullemer, B., and Riehl, N. 1966. Bulk and surface conductivity of ice. *Solid State Communications*, Vol. 4, No. 9, p. 447-48.
- Bullemer, B., and others. 1969. Protonic conduction in ice. Part I: high temperature region, [by] B. Bullemer, H. Engelhardt, N. Riehl. (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. 416-29.)
- Carslaw, H. S., and Jaeger, J. C. 1959. *Conduction of heat in solids*. Second edition. Oxford, Clarendon Press.
- Davy, J. G., and Samorjai, G. H. 1971. Studies of the vaporization mechanism of ice single crystals. *Journal of Chemical Physics*, Vol. 55, No. 8, p. 3624-36.
- Delaney, L. J., and others. 1964. The rate of vaporization of water and ice, by L. J. Delaney, R. W. Houston and L. C. Eagleton. *Chemical Engineering Science*, Vol. 19, No. 2, p. 105-14.
- Eigen, N., and others. 1964. Über das kinetische Verhalten von Protonen und Deuteronen in Eiskristallen, von M. Eigen, L. DeMaeyer und H.-C. Spatz. *Berichte der Bunsengesellschaft für physikalische Chemie*, Bd. 68, Nr. 1, p. 19-29.
- Fletcher, N. H. 1968. Surface structure of water and ice. II. A revised model. *Philosophical Magazine*, Eighth Ser., Vol. 18, No. 156, p. 1287-300.
- Jaccard, C. 1959. Étude théorique et expérimentale des propriétés électriques de la glace. *Helvetica Physica Acta*, Vol. 32, Fasc. 2, p. 89-128.
- Jaccard, C. 1967. Electrical conductivity of the surface layer of ice. (In Ōura, H., ed. *Physics of snow and ice: international conference on low temperature science. . . . 1966. . . . Proceedings*, Vol. 1, Pt. 1. [Sapporo], Institute of Low Temperature Science, Hokkaido University, p. 173-79.)
- Jelinek, H. H. G. 1967. Liquid-like (transition) layer of ice. *Journal of Colloid and Interface Science*, Vol. 25, No. 2, p. 192-205.
- Kvlividze, V. I., and others. 1974. The mobile water phase on ice surfaces, [by] V. I. Kvlividze, V. F. Kiselev, A. B. Kurzayev and L. A. Ushakova. *Surface Science*, Vol. 44, No. 1, p. 60-68.
- Maeno, N. 1973[a]. Measurements of surface and volume conductivities of single ice crystals. (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. 140-43.)
- Maeno, N. 1973[b]. Single crystals of ice grown from KCl solution and their dielectric properties. *Canadian Journal of Physics*, Vol. 51, No. 10, p. 1045-52.
- Maidique, M. A., and others. 1971. Transfer of protons through "pure" ice I_h single crystals. III. Extrinsic versus intrinsic polarization; surface versus volume conduction, [by] M. A. Maidique, A. [R.] Von Hippel and W. B. Westphal. *Journal of Chemical Physics*, Vol. 54, No. 1, p. 150-60.
- Mason, B. J., and others. 1963. The growth habits and surface structure of ice crystals, by B. J. Mason, G. W. Bryant and A. P. Van den Heuvel. *Philosophical Magazine*, Eighth Ser., Vol. 8, No. 87, p. 505-26.

DISCUSSION

J. G. PAREN: You have discussed the d.c. response of ice surfaces. Have you tried to measure the a.c. response as well? Do you know if ice surfaces have a dielectric response?

N. MAENO: We have tried to measure a.c. responses of the ice surface with the present electrode system, but the analyses are not completed yet. I think that ice surfaces have a dielectric response, and that it could give more information about the surface properties of ice.

C. JACCARD: What is the temperature dependence of the "anomalous" component of the conductivity due to the quasi-liquid layer between 0 and -10°C ?

MAENO: We think that the "anomalous" excess component of the surface conductivity observed near the melting point is caused by the conduction in the quasi-liquid layer formed on the ice surface, so that the temperature dependence of the component is considered to be in accordance with that of the thickness of the layer.

J. HALLETT: The structure of any liquid-like layer on the ice surface is a function of temperature as has been suggested before, but would also be expected to be dependent on the outlying vapour pressure. You have shown that it is sensitive to evaporation rate through surface temperature. How good is your assessment of surface temperature and ambient vapour pressure?

MAENO: I agree. We measured the surface temperature with a 0.1 mm diameter copper-constantan thermocouple to an accuracy of 0.05 deg, and all the experiments were conducted after saturation of water vapour had been attained. We do not think any supersaturated water vapour existed above the ice surface.

K. ITAGAKI: Could you suggest some possible mechanism for the abrupt increase of conductance coupled with the decrease in surface temperature?

MAENO: The increase of surface conduction on the subliming ice surface is considered to be attributable to the formation of any electrically active defects in the surface region due to sublimation, and the decrease to the surface cooling due to sublimation.

P. CAMP: Have you any model in mind for the process? My reason for asking is this: Some years ago we made surface measurements which gave both high activation energy and high conductivity (Camp and others, 1967). Using reasonable values of hopping times and charge, we found we could not have both large activation energy and large values of conductivity for a monolayer. However, when we relaxed the condition of true surface conductivity and considered conduction in a thin surface region, we no longer had this difficulty because we could assign two parts to our activation energy. One of these was the activation energy for the proton motion and the other that for the film thickness.

MAENO: From our experimental results we can give a tentative model for the surface conduction of ice. We consider that two different mechanisms are essentially responsible for the observed results: One is the surface conduction having the temperature-independent activation energy (1.43 eV), which is predominant at lower temperatures below -6°C , and the other is the appearance of the quasi-liquid layer, which is superimposed on the first and is predominant at higher temperatures, above -6°C (see Fig. 2). We agree with you that the observed surface conduction cannot be explained as occurring only in a surface monolayer. It seems more probable that the surface conduction of ice is a phenomenon taking place in a surface layer with some effective thickness in which the molecular structure is disordered in the sense that it is not as completely crystalline as the bulk ice. If we assume that the effective thickness of the surface layer is δ and that the charge carriers are only of one kind, possibly H_3O^+ , the surface conductivity σ is written as

$$\sigma = \delta n \eta q, \quad (1)$$

where n , η , and q are respectively the concentration, mobility, and effective charge of the charge carrier. It should be noted in Equation (1) that δ , n , and η are functions of temperature.

At temperatures below -6°C observed values of σ obeyed the Arrhenius equation, so if the above three quantities are represented in the form of $\exp(-E/kT)$, the large experimental value of activation energy can be decomposed as

$$E_{\delta} + E_n + E_{\eta} = 1.43 \pm 0.09 \text{ eV}, \quad (2)$$

where E_δ , E_n , and E_η are components which are associated with the layer thickness, carrier formation, and mobility, respectively. We have not enough information to separate each of them further, and the effects of relaxation time for surface molecules and drift distance should also be taken into consideration. At temperatures above -6°C , δ in Equation (1) is approximately equal to the thickness of the quasi-liquid layer covering the ice surface, and we suppose that the enormously large temperature dependence of surface conductivity in this region is attributable to that of δ as I have already mentioned briefly in response to Professor Jaccard's question.

REFERENCE

- Camp, P. R., and others. 1967. Electrical conduction in ice, by P. R. Camp, W. Kiszénick and D. A. Arnold. *U.S. Cold Regions Research and Engineering Laboratory. Research Report 198.*