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Thermoelectric Properties of Ice

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Abstract

The thermoelectric potential difference produced at both ends of an ice rod under a temperature gradient was measured on single crystal ice obtained at the Mendenhall glacier and ice formed in solutions of hydrofluoric acid. At temperatures lower than $-10°C$ or thereabouts, the cold end of ice rod made of single crystal ice acquired a positive charge and H_3O^+ ion was considered to be the primary charge carrier. At temperatures higher than $-10°C$ or thereabouts, the cold end gained a negative charge and L-defects were considered to be the main charge carrier. The results obtained in this experiment were different from those of Latham and Mason, especially at high temperatures.

I. Introduction

Experimental and theoretical studies of defects in ice have been carried out intensively by many workers during recent years. Ionic defects of H_3O^+ and OH^- have been considered in ice crystals analogically based on ionic defects in water. Bjerrum (1952) suggested the existence of an orientational defects in order to explain the large dielectric constant of ice. Electrical properties of these ionic and orientational defects have been studied by the measurements of dielectric constant (Steinemann and Gränicher, 1957; Steinemann, 1957), the measurements of the electric conductivity (Decroly *et al.*, 1957; Bradley, 1957; Jaccard, 1959; Gross, 1962; Heinmets and Blum, 1963; Chai and Vogelhut, 1965), thermoelectric measurements (Latham and Mason, 1961; Bryant and Fletcher, 1965), and by theoretical studies of thermoelectricity (Jaccard, 1963, 1964).

The nature of hydrogen bond in defects has been investigated theoretically (Lennard-Jones *et al.*, 1951; Roothaan, 1951; Duncan and Pople, 1953; Conway *et al.*, 1956; Buckingham, 1958; Cohan *et al.*, 1962; Weissmann, 1965).

The measurement of the thermoelectric power of ice is one of the best means to determine which defect is more effective in producing a potential difference for given temperatures. This measurement gives information for each behavior of positive electric defect and negative electric defect, and that of activation energies of these defects. As it was very difficult to discuss the electric properties of defects from the measurement of thermoelectric power of polycrystalline ice used by Latham and Mason (1961) and Bryant and Fletcher (1965), single crystal ice was used in this experiment.

II. Experimental Apparatus

A rod of single crystal ice was prepared from the Mendenhall glacier ice of Alaska, and two palladium disks were frozen to both ends of the rod at a temperature near the

freezing point. The specific electric conductivity of this ice rod was $2.2\,\mu\mho\,cm^{-1}$. The dimension of the ice rod was 3~5 cm in length and 1 cm² in its cross section. A platinum wire was connected to the upper palladium disk and a platinum-platinum rhodium wire was welded to the lower palladium disk by a spotwelder. The upper platinum wire was grounded and the lower platinum wire was connected to a vibrating reed electrometer. The temperature of the upper surface of the ice rod was measured by a copper-constantan thermocouple and that of the lower surface was measured by a platinum-platinum rhodium thermocouple. The platinum-platinum rhodium wire was only used when the temperature of the lower end was measured. A temperature difference of 10°C was maintained at both ends of the sample by electric heaters.

In order to minimize any electrification of the insulator due to temperature variation, insulators were used only at the top of this apparatus and the temperature of these insulators were kept constant by the electric heaters.

After the palladium disks were frozen to the ice rod in a cold room, this apparatus was placed in a stainless steel vessel and was sealed tightly by the use of metal packing and was cooled to −50°C with dry ice (Figs. 1 and 2). Experiments were performed
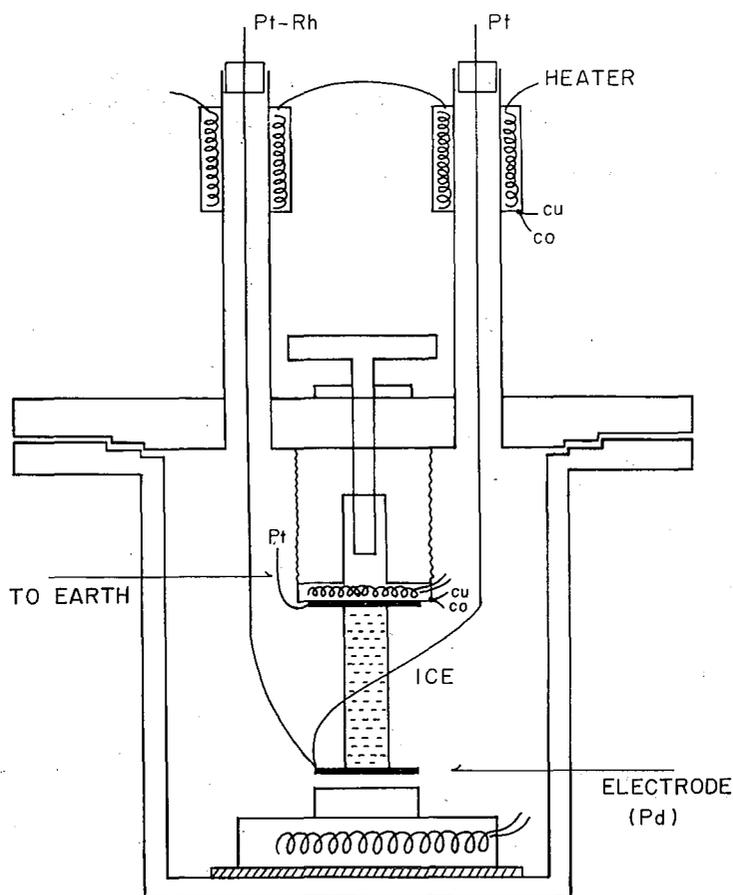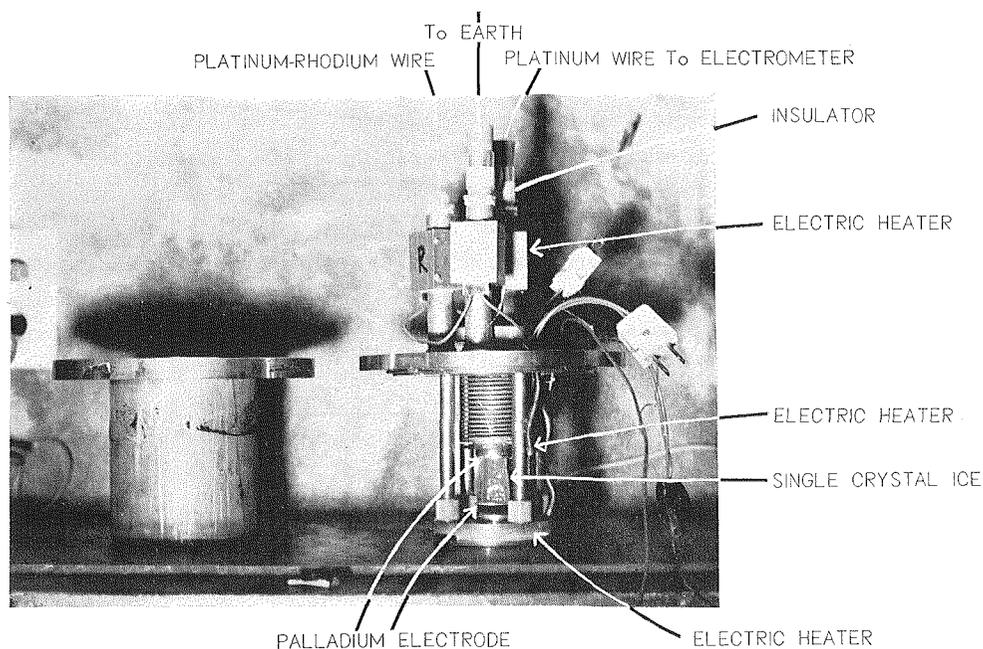

Fig. 1. Experimental apparatus

Fig. 2. Experimental apparatus

after annealing for 3 days at $-3°C$ in the cold room. $20 \sim 30$ mV of the potential differ-
ence were usually found even when no temperature gradient was applied through the
ice sample, and this value varied with the temperature at the beginning of the experiment.
However, after annealing for 3 days, the potential difference became independent of the
temperature.

III. Experimental Results

As some complicated results due to unknown electrical behaviors of defects existing
in single crystal ice were expected, we measured the thermoelectric potential of ice
samples doped with hydrofluoric acid at the onset of the experiment. The electrical
properties of ice doped with HF have been clarified by several authors. Steinemann
(1957) has shown by the measurement of dielectric constant of ice that H_3O^+ ion defect
plays an important role on the electrical properties of ice doped with diluted hydrofluoric
acid $(5 \times 10^{-3}$ N) but L-defect becomes important when ice contains much larger hydrofluoric
acid content $(5 \times 10^{-1}$ N). For the above extreme cases, only one kind of charge carrier,
H_3O^+ or L-defect, may govern the thermoelectric power of ice, and this power may be
determined by the equation $|dV/dT| = E/2eT$, where E is the enthalpy and e the electric
charge of an electron. The results of thermoelectric power of these ice samples are
shown in Fig. 3. The ordinate is the potential difference between the cold and warm
ends of ice rod divided by the temperature difference between the two ends and the
abscissa shows the mean temperature of the ice rod. In the case of ice containing
5×10^{-3} N of HF acid, the sign of the potential of the cold end was always kept positive
irrespective of the temperatures, and this experimental result fits the theoretical curve
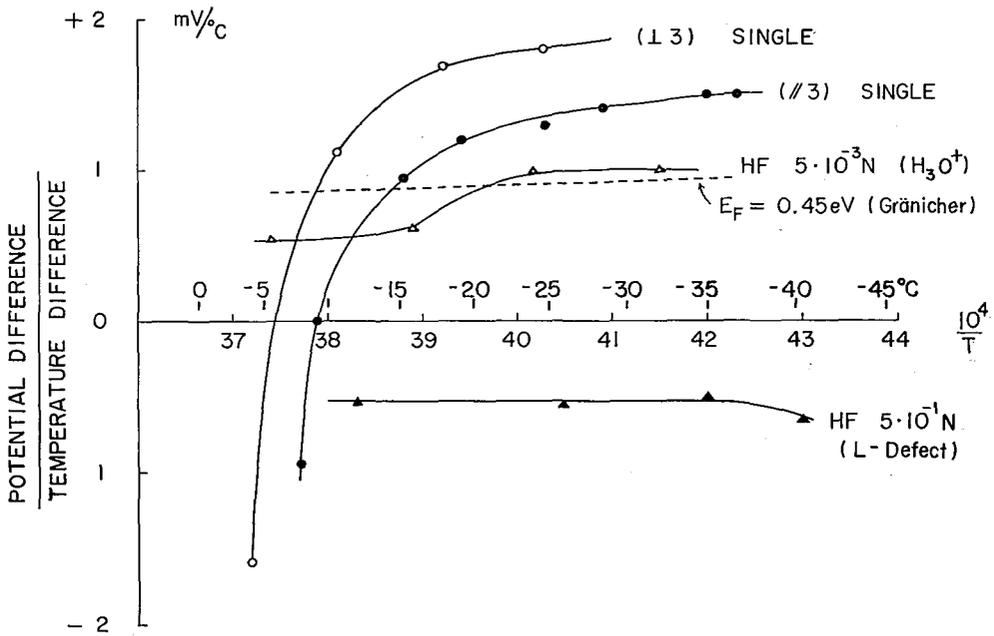
Fig. 3.　Thermoelectric power of ice containing hydro-fluoric acid
(5×10⁻³ N, 5×10⁻¹ N) and single crystal ice

$|dV/dT| = E/2eT$, where E is taken as the activation energy of the H_3O^+ ion. The value of E was obtained as 0.45 eV by Steinemann (1957) and Jaccard (1959). From this result, it may be considered that the change of the temperature of the electrodes did not exert any influences on the measurment of the thermoelectric power of ice. In the case of ice doped with 5×10^{-1} N acid, the sign of potential of the cold end was always maintained negatively irrespective of the temperatures. This result may be explained
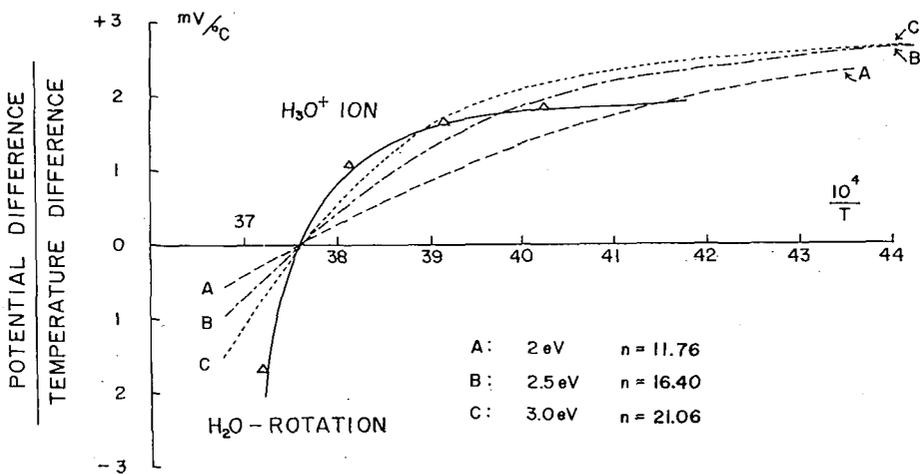

Fig. 4.　Thermoelectric power of single crystal ice. Dotted lines are
theoretical curves as a function of activation energy of L-defect
at warmer temperature

by the assumption that the L-defect is the negative charge carrier and this defect may transfer the charge toward the cold end of the ice rod.

The thermoelectric power of single crystal ice prepared from the Mendenhall glacier ice of Alaska are shown in Fig. 4. At temperatures warmer than about $-10°C$, the cold end of the ice rod became negative and the absolute magnitude of the potential difference produced at both ends increased with the increasing temperature. At temperatures colder than $-10°C$ or thereabouts, the cold end was electrified positively and its magnitude decreased gradually with the increasing temperature.

In comparison with the above results with those for HF-doped ice, it may be considered that the H_3O^+ ion behaves predominantly as the charge carrier in the single crystal ice in a low temperature range, while the L-defect behaves predominantly as the charge carrier in a high temperature range.

In order to extend the measurement of thermoelectric power of ice to the temperature range lower than $-40°C$, a new method was used for preparation of the electrodes. In the previous measurements, the palladium disks were frozen directly to both ends of an ice rod as the electrodes. When temperature was lowered to $-40\sim-60°C$, sometimes several cracks were formed in ice in the vicinity of two electrodes because of the difference of thermal expansion coefficient between an ice and a palladium disk. To avoid this crack formation near the electrode, some palladium powder was inserted between palladium disks and ice rod. The palladium powder provided a perfect electrical conduction and contact between electrode and ice specimen and allowed a reliable measurement of thermoelectric power of ice to the temperature of $-60°C$ without any trouble due to crack formation. In this case an electrical insulator which consists of polystyrene
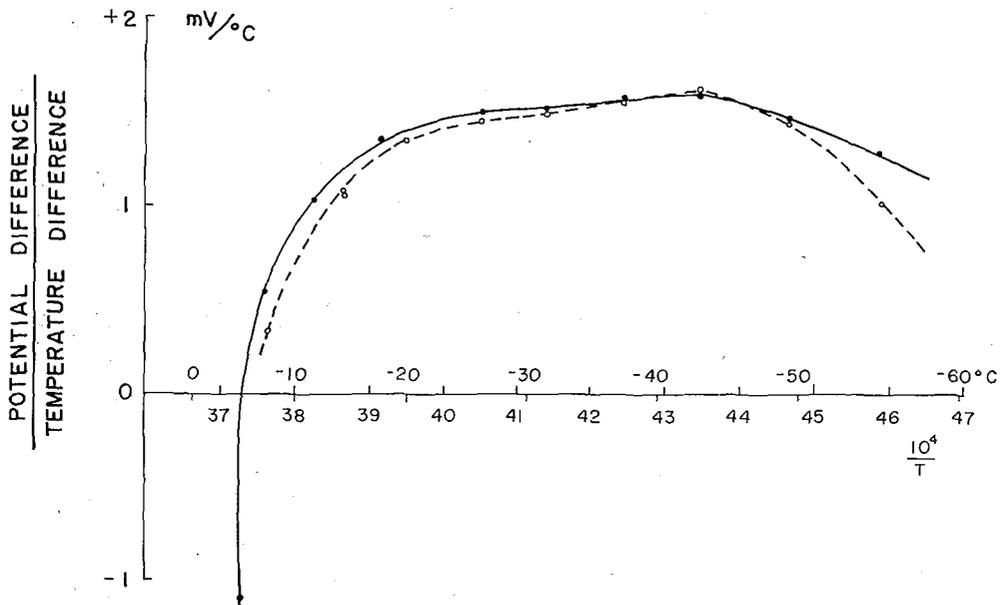

Fig. 5. Thermolectric potential obtained by the use of samples of Mendenhall glacier. New method was used for measuring the thermoelectric potential until lower temperature

disk was placed underneath the lower electrode to ensure contact between the powder and the electrode and to keep them from electrical leakage.

Figure 5 shows the temperature dependence of the thermoelectric potential of single crystal ice measured by this powder-electrode method. The sample was prepared from an ice block obtained at the Mendenhall glacier. As seen in this figure, the result was nearly the same as the previous one obtained at higher temperatures than −40°C. At lower temperatures than −50°C, thermoelectric power decreased with decreasing temperature. This fact suggests that the effect of negative charge carrier becomes predominantly at low temperature range. This negative can be considered to be the extrinsic L-defect.

IV. Consideration

Bradley (1952) measured the electric conductivity of ice and showed that the values of electric conductivity near the freezing temperature deviated from those of lower temperatures. The results obtained by Bradley (1952) and Jaccard (1959) are plotted logarithmically against T^{-1} in Fig. 6. The deviation of the values of the electric conductivity from the straight line suggests the coexistence of another type of defect having a still larger activation energy near the freezing temperature. At near freezing temperature the rotation of H_2O molecule is considered as one of these possibilities, where four hydrogen bonds are broken and three hydrogen bonds remain in a hanging state. The rotation of H_2O may more easily occur in such a way that a L-defect is produced at
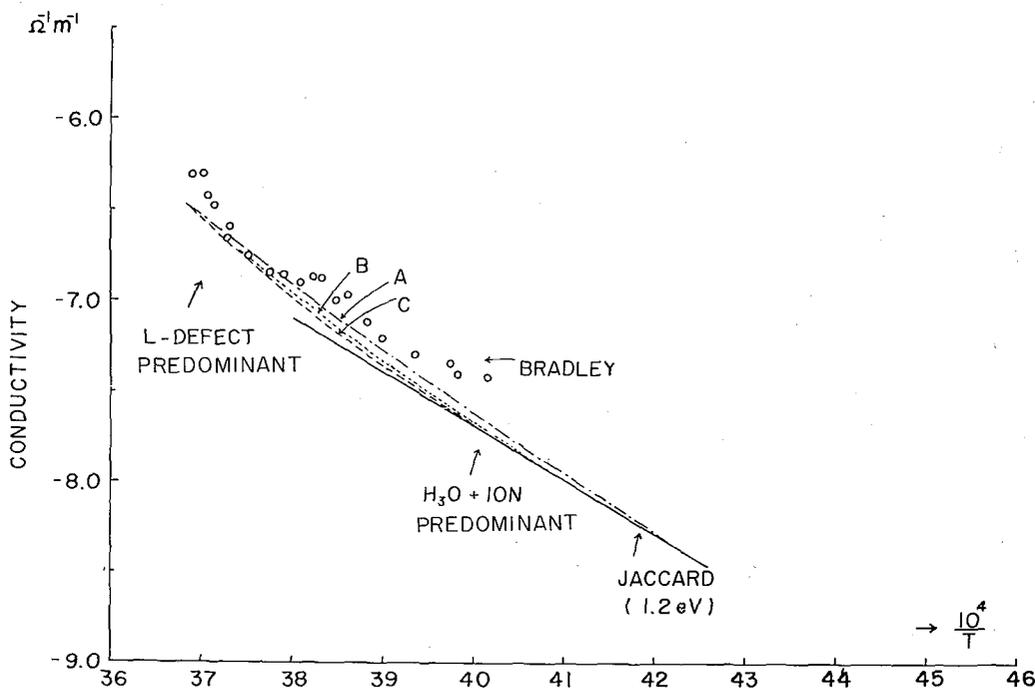

Fig. 6.   Electric conductivity of ice. Dotted lines show conductivities composed of two different electric charge carriers

A: $10^{11.76}\, e^{-\frac{2eV}{2kT}}$,   B: $10^{16.40}\, e^{-\frac{2eV}{2kT}}$,   C: $10^{21.06}\, e^{-\frac{2eV}{2kT}}$

one rebinding bond, because the activation energy to create D-defect is 2 eV higher than that of the excess L-defect as shown by the calculations of Conway *et al.* (1956). These additional defects produced near the freezing temperature may cause an abrupt increase of the electric conductivity.

At lower temperatures, ionic defects are considered to be more effective than L-defects. According to Eigen *et al.* (1956), the ratio of mobility of H_3O^+ ion and OH^- is 10~100. Therefore, H_3O^+ ion may have a predominant effect on thermoelectricity in a low temperature region.

When two kinds of charge carriers exist in an ice crystal, the thermoelectric power may be written as

$$\frac{dV}{dT} = \frac{\sigma_1 S_1 + \sigma_2 S_2}{\sigma_1 + \sigma_2} ,$$

$$\sigma_1 = 10^{n_1} e^{-\frac{E_1}{2kT}} , \qquad \sigma_2 = 10^{n_2} e^{-\frac{E_2}{2kT}} ,$$

where σ_1, and σ_2 are the electric conductivity of charge carriers 1 and 2, S_1 and S_2 are the thermoelectric power of charge carriers 1 and 2 respectively. n_1 and n_2 are numerical values.

From the measurement of the electric conductivity of ice by Jaccard, σ_2 is written as

$$\sigma_2 = 10^{4.4} e^{-\frac{1.2 eV}{2kT}} ,$$

at low temperature. In order to correlate the experimental values of conductivity of ice near the freezing temperature obtained by Bradley with those of low temperatures obtained by Jaccard, additional conductivity σ_1 was introduced as a function of n_1 and of E_1 where n_2 and E_2 were chosen to be constant as 4.4 and 1.2 eV. Figure 4 represents the comparison between our experimental results and calculated values. Curves A, B and C were calculated, using the following values:

$$E_1 = 2 \text{ eV} \qquad n_1 = 11.76 \qquad \text{for curve A},$$
$$E_1 = 2.5 \text{ eV} \qquad n_1 = 16.40 \qquad \text{for curve B},$$
$$E_1 = 3.0 \text{ eV} \qquad n_1 = 21.06 \qquad \text{for curve C}.$$

As can be estimated from this figure, the value of activation energy of the excess rotation of L-defect ranges between 2~3 eV. The result obtained from the consideration of the additional conductivity σ_1 is shown in Fig. 3.

V. Conclusion

The thermoelectric potential produced at both ends of an ice rod was measured over a wide range of temperatures, using a single crystal ice and samples doped with hydrofluoric acid.

For single crystal ice the potential of the colder end of ice rod was found to be negative in the range of temperature higher than −10°C or thereabouts, but the sign was reversed in the temperature range lower than −10°C. The primary charge carriers in the high temperature range may be considered to be the excess rotation of L-defects produced by the rotation of H_2O molecules, while charge carriers in the low temperature range may be H_3O^+ ions. These results may be favorable for the explanation of showers

composed of positively electrified graupel observed frequently in nature and the positively electrified rime type found by Magono and Takahashi (1963) in their laboratory experiments.

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