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Title	Studies of the Dielectric Properties of Ice Grown from KCl Solution
Author(s)	MAENO, Norikazu; 前野, 紀一
Citation	Contributions from the Institute of Low Temperature Science, A25, 1-47
Issue Date	1973-07-31
Doc URL	https://hdl.handle.net/2115/20237
Type	departmental bulletin paper
File Information	A25_p1-47.pdf

Studies of the Dielectric Properties of Ice Grown from KCl Solution[*]

By

Norikazu MAENO

前 野 紀 一

The Institute of Low Temperature Science

Received May 1973

Abstract

Polycrystals and monocrystals of ice were grown from KCl solutions and their dielectric properties were investigated as functions of frequency, temperature, concentration, grain size and thickness of each specimen. When the temperature was higher than the eutectic point of the KCl–H_2O system ($-10.7°C$) the presence of the liquid solution gave considerable effect on the dielectric properties of the polycrystalline KCl ice, showing extremely large values of dielecric constant and conductivity.

At temperatures lower than $-10.7°C$ contributions from the liquid phases vanished, but fairly complicated modifications appeared in the dielectric properties due to the KCl impurity segregated mainly at grain boundaries. In the high-concentration ice ($>10^{-2}M$), two types of dielectric dispersions were observed: one appeared at higher frequencies than that of the orientational polarization in pure ice, which could be fitted by Debye's equations and had an activation energy of 5.3 kcal/mol; the other appeared at much lower frequencies, being widely distributed. In the low-concentration ice ($<10^{-2}M$) the dielectric dispersion was observed to extend over a significantly wide range of frequency and show large values of dielectric constant and conductivity.

It was shown that chlorine ions were only incorporated in the crystal lattice of ice when a single crystal of ice was grown from a dilute KCl solution. The upper limit of the chlorine incorporation was approximately $1\times10^{-4}M$. The incorporation of chlorine decreased the value of dielectric constant and the activation energy of dielectric relaxation (5.76 kcal/mol). The low-frequency conductivity increased as the square root of the chlorine concentration, and its activa-

tion energy was 6.1 kcal/mol. These experimental results were discussed in terms of the lattice defects created in the ice crystal.

<div style="text-align: center">Contents</div>

I.   Introduction

The detailed knowledge of electrical properties of impure ice is greatly demanded in the research fields of glaciology, such as the propagation measurements of radio waves in the polar regions (Yoshino 1961), the electrical resistivity soundings of ice thickness and crevasses (Röthlisberger 1967), and the radio-echo sounding of the depths of ice sheets (Evans 1963, 1966), since the natural ices investigated in these measurements contain various kinds of chemical impurities to some extent. So far the electrical properties of pure ice have been extensively studied to inquire into the molecular structure in special reference to the proton jumps in the crystal lattice (Auty and Cole 1952, Humbel et al. 1953, Gränicher et al. 1957, Onsager and Dupuis 1962). The electrical properties of impure ice containing HF (Steinemann 1957, Jaccard 1959) or NH₄F (Zaromb and Brill 1956,

BRILL *et al.* 1957) were also investigated to find out their effects on the orientational polarization of H_2O molecules in ice. The concentration of fluorides, however, may be almost ignored in the natural ices, in which the most abundant impurities are considered to be chlorides. Typical among the natural ices containing chlorides is sea ice, and its main impurities are NaCl, $MgCl_2$, KCl and so forth (ASSUR 1958).

Recently several authors measured the dielectric properties of sea ice as functions of frequency and temperature (FUJINO 1967a, 1967b, ADDISON and POUNDER 1967, ADDISON 1969). They reported that the values of dielectric constant and conductivity were extremely large in comparison with those of pure ice and wide dispersions of these values occurred in the range of audio frequencies. The values of dielectric constant and conductivity measured at 10^2 Hz and $-10°C$, for instance, were 10^6 and 0.1 mho/m, while those of pure ice were 95 and 3.4×10^{-8} mho/m, respectively. The notable finding in their investigations was that, when the temperature of sea ice was lowered, the values of dielectric constant and conductivity changed abruptly at the specific temperatures of $-22.9°C$ (the precipitation temperature of $NaCl \cdot 2H_2O$) and $-55°C$ (the eutectic temperature of sea ice). From these results, it has been concluded that the liquid brine plays important roles in the dielectric properties of sea ice. When the temperature of sea ice was below the eutectic point, the liquid brine existed no longer within the ice and turned to solid $NaCl \cdot 2H_2O$ and other eutectic compounds, so that the values of dielectric constant and conductivity decreased discontinuously at the specific temperature. In general the value of dielectric constant of sea ice is not simply proportional to the apparent concentration of impurities. This implies that the natural sea ice cannot be treated as a simple mixture dielectric substance composed of brine inclusions and pure ice. It has been accepted that fluorides such as HF and NH_4F can be incorporated in ice in the form of solid solution and modify the dielectric properties of ice. Several authors reported recently the possibility of the incorporation of chlorides in the ice crystal lattice (KUROIWA 1965, YOUNG and SALOMON 1968, NAKAMURA and JONES 1970). When ice is formed in water containing chlorides, the major part of the solutes is rejected, but some amount is segregated at grain boundaries and also incorporated within the ice lattice. The effects the segregated chlorides exert on the dielectric properties are considered to be different from those of the incorporated ones in the ice lattice.

The present author has attempted to investigate the dielectric properties of impure ice containing a single component of chemical impurity, KCl, in

a wide range of frequency, temperature and concentration. KCl was chosen because the eutectic temperature of the KCl–H$_2$O system was relatively higher than that of NaCl and others. The dielectric properties of polycrystalline KCl ice at temperatures above and below the eutectic point are discussed in Chapters II and III, respectively, in relation to contributions from the impurities segregated at grain boundaries. In Chapter IV, the dielectric properties of single crystals of ice grown from KCl solution are discussed as regards the preferential incorporation of chlorine in the ice lattice.

II.   Dielectric properties of KCl ice above
the eutectic temperature

II. 1.   *Phase relations of the KCl–H₂O system*

The aqueous solution of KCl has been widely used as a standard solution for the measurement of electrical conductivity of various solution, since KCl dissociates almost completely in water. Figure 1 shows the phase diagram for the KCl–H$_2$O system (WASHBURN 1928). The eutectic point is specified by the temperature of $-10.7°C$ and the KCl concentration of $3.3\,M$ (g·mol/l), at which the ice, KCl solution and KCl crystal can coexist in thermodynamical equilibrium. The diagram shows that the liquid phase can only exist in KCl ice at temperatures higher than $-10.7°C$, while all of the KCl impurity is included in the forms of solid particles at lower temperatures.

When a KCl solution is cooled to produce KCl ice, the distribution of KCl in the resulting ice is not generally uniform. It is usually entrapped in the forms of brine pockets between thin ice platelets or at grain boundaries. The reason for this is that the distribution coefficient of KCl is small in ice. It will be shown in Chapter IV, however, that when a single crystal of ice is grown from KCl solution, some amount of chlorine is preferentially incorporated in the ice lattice, producing a kind of solid solution.
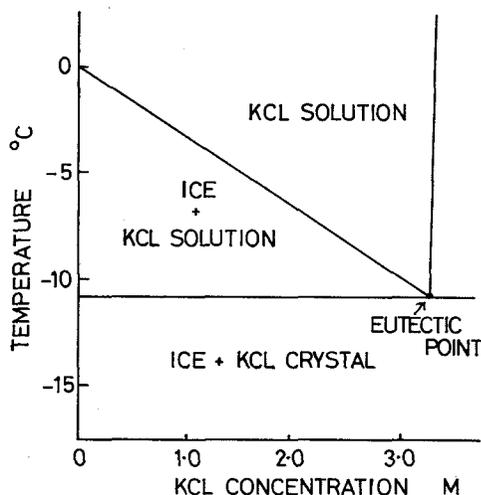

Fig. 1. Phase diagram of the KCl–H$_2$O system. Only the high H$_2$O portion is shown

When the temperature of KCl ice is lowered, the concentration of KCl in the entrapped brine pockets increases due to the precipitation of ice. The volume fraction, v, of KCl solution in an N M KCl ice, which is in equilibrium at a given temperature above the eutectic point, can be written as

$$v = \frac{N/N_0}{N/N_0 + (\rho - \rho_0 N/N_0 - 0.0746\,N)/\rho_i}, \qquad (\text{II. 1})$$

where N_0 and ρ_0 are the equilibrium concentration (M) and density (kg/l) of the KCl solution at the temperature, and ρ_i and ρ are the densities (kg/l) of the ice and N M KCl solution. This equation was obtained by assuming that no air inclusions were contained in the KCl ice.

II. 2. *Preparation of specimens and devices for measurements*

A specimen of KCl ice was obtained by freezing some 50 cm³ of KCl solution in a Plexiglas tube of 7.5 cm in diameter as shown in Fig. 2.a. Freezing proceeded unidirectionally from the bottom when the tube was placed in a cold room at −22°C. The growth rate of ice was controlled with an electric heating tape wrapped along the outer surface of the tube so that the KCl distribution might be as uniform as possible in the specimen. When the freezing of the entire KCl solution was completed, the KCl ice was taken out of the tube and inserted between the two gold-evaporated copper electrodes (each 7.5 cm in diameter, Fig. 2.b) in the cold room. Since the surfaces of the electrodes were previously warmed just above 0°C slight melting occurred at the surfaces of the specimen, but this
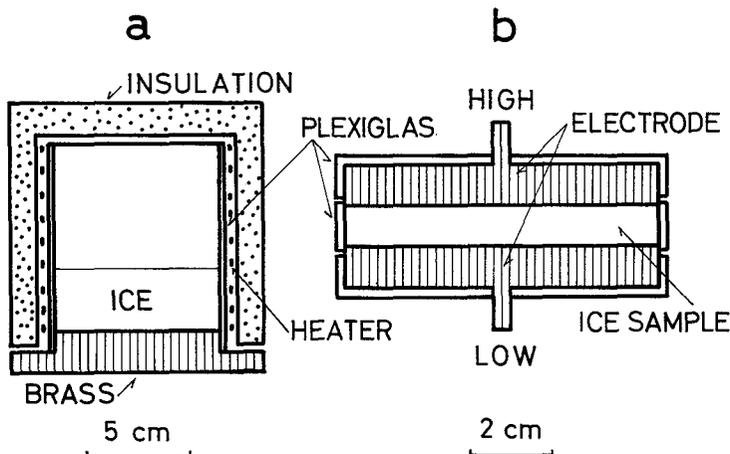

Fig. 2. Device for growing KCl ice (a) and the dielectric cell (b)

melt froze rapidly making close contact between the specimen and the electrodes. The Plexiglas ring was used to avoid bleeding of the melted solution and evaporation of the specimen during the measurement. Though the heterogeneous distribution of impurity was inevitable in the specimen thus formed, no KCl was lost during the preparation. Therefore, it may be assumed that the average KCl concentration of the specimen is equal to that of the original solution, which was verified later by measuring the electrical conductivity of the melted specimen.

When the KCl concentration was less than about 10^{-3}M the ice specimen was usually trasparent and no visible air bubbles were entrapped, but ice specimens formed from higher concentration solution were opaque and many liquid inclusions and air bubbles were entrapped. These brine inclusions were captured between thin ice platelets and the appearance of such KCl ice was very similar to that of natural sea ice. These inclusions seemed to orient in the direction of growth.

The temperature of the specimen could be varied from 0°C to −33°C. Electrical measurements were conducted after a complete thermal equilibrium was attained by keeping the KCl ice capacitor at a given temperature for about 10 hours. Rapid changes of temperature were avoided to prevent the ice specimen from cracking.

The electrical measurements were made in a frequency range from 50 Hz to 2×10^4 Hz by using a General Radio 1603–A Z–Y bridge and a 1232–A tuned null detector. The relative dielectric constant, κ', loss factor, κ'', and conductivity, σ, of an ice specimen were calculated from the following definitions :

$$\kappa' = C_x/C_0 , \tag{II. 2}$$

$$\kappa'' = G_x/\omega C_0 , \tag{II. 3}$$

and

$$\sigma = \varepsilon_0 G_x/C_0 , \tag{II. 4}$$

where C_x and G_x are the measured equivalent parallel capacitance and conductance of the specimen, C_0 is the geometrical capacitance of the condenser with a vacuum between the electrodes, ω is the angular frequency of the applied alternating field, and ε_0 is the dielectric constant of free space $(=8.854 \times 10^{-12}$ farad/m). Since κ' and κ'' are the real and imaginary parts of a complex dielectric constant, κ^*, they can be represented as follows :

$$\kappa^* = \kappa' - i\kappa'' , \tag{II. 5}$$

where $i = \sqrt{-1}$.

II. 3. *Results and interpretations*

Figure 3 shows the temperature dependences of dielectric constant and conductivity of 0.1 M ice measured at 2×10^2 Hz, 2×10^3 Hz and 2×10^4 Hz. The values of dielectric constant and conductivity increased as the temperature was raised, showing sharp discontinuities at a specific temeprature around $-11°$C. As seen in Fig. 1, this temperature is regarded to be the eutectic point of the KCl–H$_2$O system. The general aspect of the temperature dependence of dielectric constant is quite similar to that found in sea ice (FUJINO 1967a, 1967b, ADDISON and POUNDER 1967, ADDISON 1969). Therefore, the liquid phase plays evidently a decisive role in the dielectric
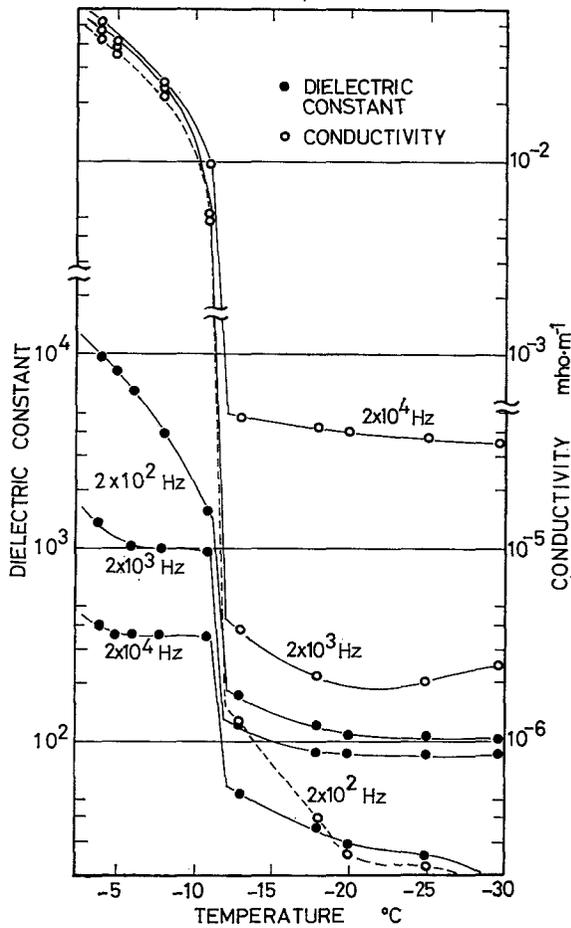

Fig. 3.   Relation between the dielectric properties of
KCl ice (10⁻¹M) and temperature

properties at temperatures above the eutectic point. The present chapter is concerned with the dielectric properties of ice containing liquid phases in a temperature range from 0°C to −11°C.

If the dielectric properties of KCl ice are simple, its dielectric constant and conductivity should increase in proportion to the content of KCl since the volume fraction of the KCl solution in ice is approximately proportional to the KCl concentration of a specimen. Figure 4 represents the dielectric constant (a), loss factor (b) and conductivity (c) of KCl ice measured at −5°C as functions of frequency and KCl concentration. Proportionality was not apparent between the dielectric constant and KCl concentration, but the values of loss factor and conductivity increased with the concentration.

Figure 5 shows the frequency dependences of the dielectric properties of 0.1 M ice as functions of temperature. The values of dielectric constant (a), loss factor (b) and conductivity (c) decreased with the lowering temperature. This can be interpreted by the continuous shrinkage of the brine volume as the temperature is lowered. A relation between the loss factor and frequency found in Fig. 5.b may be expressed by $\kappa'' \propto f^{-\lambda}$, where λ is a constant for each line in the figure. The value of λ is found to become unity as the KCl concentration or the temperature is increased. The relation, $\kappa'' \propto f^{-1}$, suggests that electrically conductive paths are provided by liquid inclusions.

Fig. 4. Frequency dependences of dielectric constant (a), loss factor (b) and conductivity (c) for KCl ice at −5°C. The parameter is the KCl concentration, and dashed lines refer to pure ice

If we assume that the entrapped KCl solution in ice is wholly distributed in the forms of cylindrical inclusions connecting the two electrodes and that the electric conduction through ice is negligible, the apparent loss factor of the KCl ice may be given by
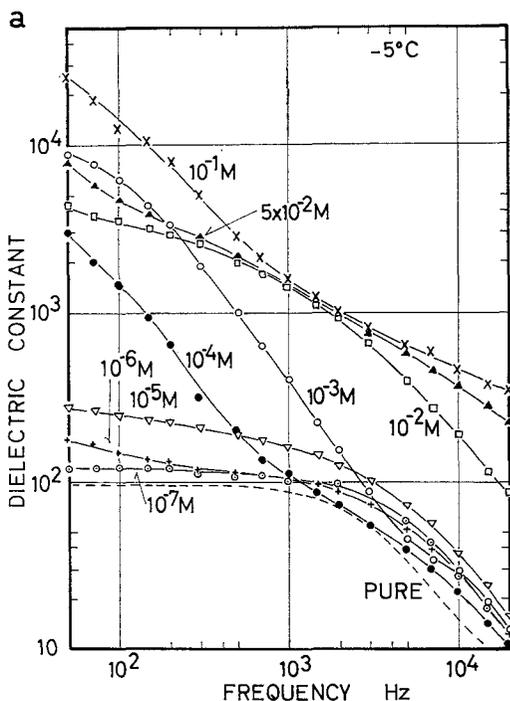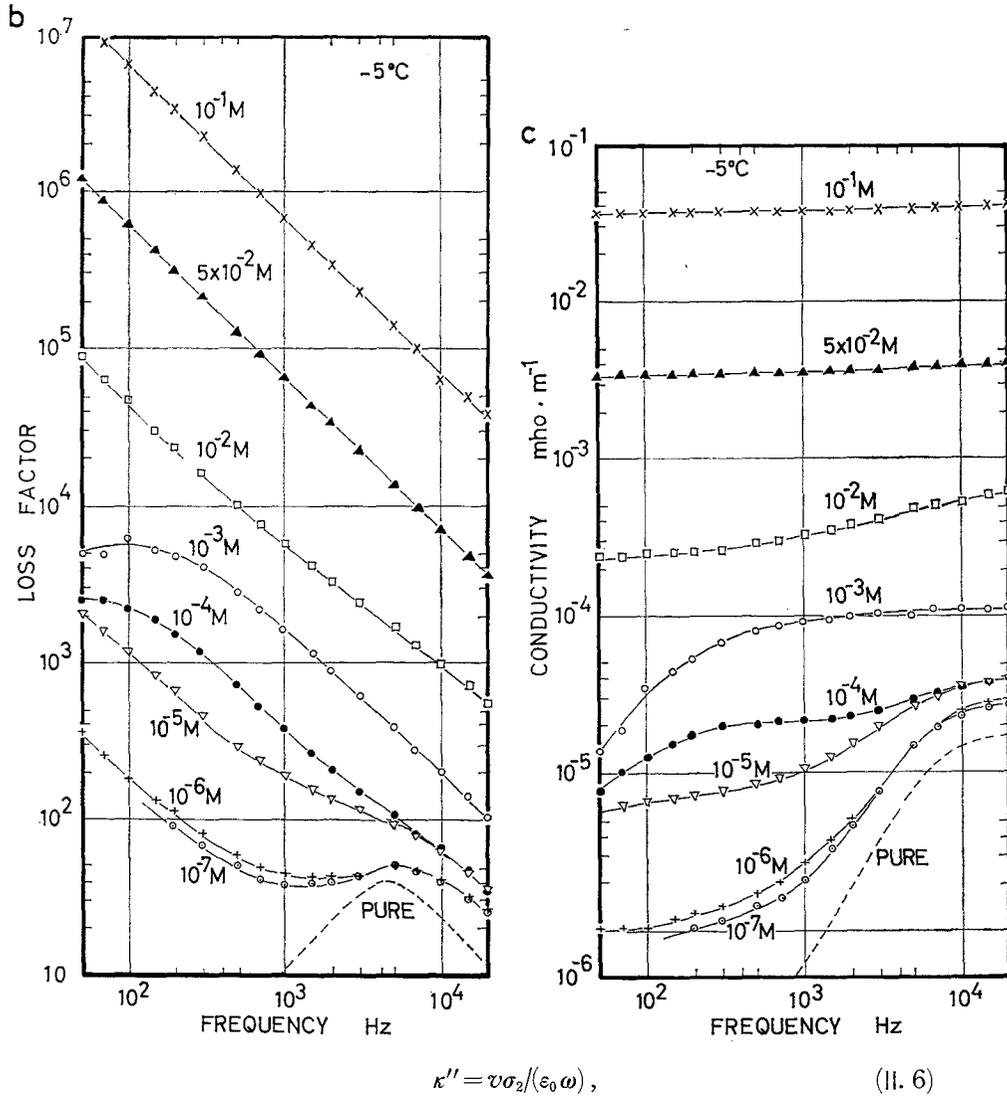
$$\kappa'' = v\sigma_2/(\varepsilon_0 \omega), \tag{II. 6}$$

where σ_2 is the electrical conductivity of KCl solution in the cylindrical inclusions, and v is the volume fraction of the solution given by Eq. II.1. The frequency dependence of κ'' was calculated for the KCl ice at $-5°C$ by using the following numerical values: $N_0 = 1.55\,M$ (the equilibrium KCl concentration at $-5°C$, WASHBURN 1928) and $\sigma_0 = 9.4\,mho/m$ which was obtained by extrapolation by using the data given in LANDOLT-BÖRNSTEIN (1960); this frequency dependence is plotted in Fig. 6. If we compare the
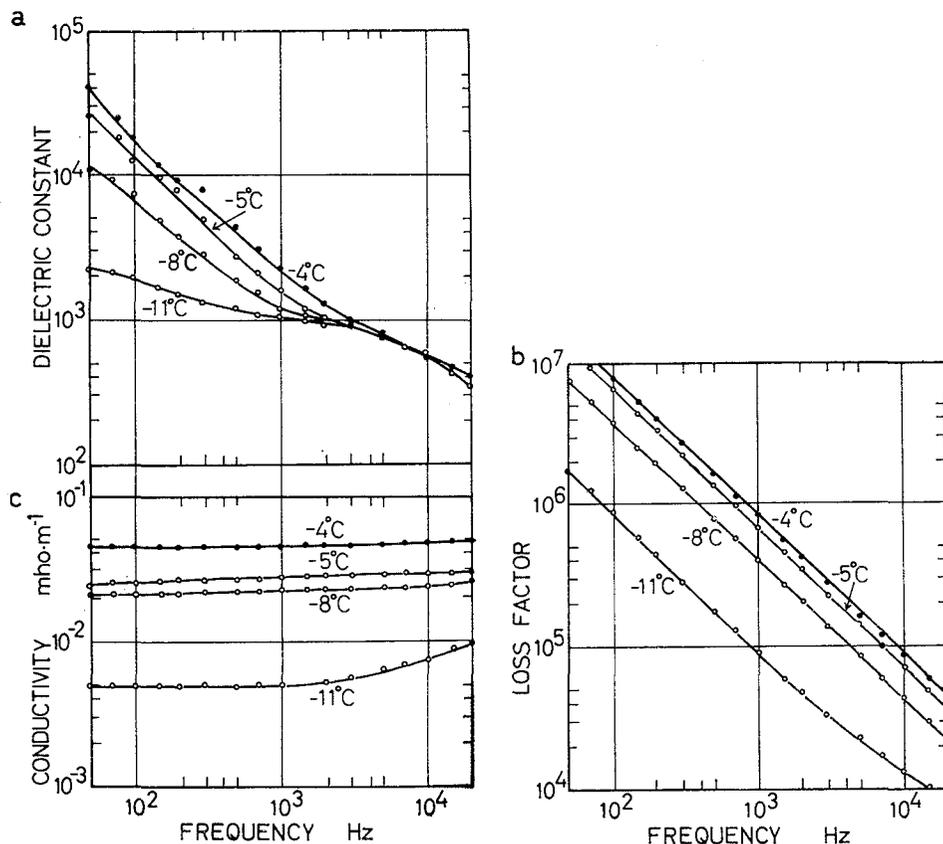
Fig. 5. Frequency dependences of dielectric constant
(a), loss factor (b) and conductivity (c) of 0.1 M ice.
The parameter is the temperature

calculated values with those obtained by the experiment, it is quite evident that the former are substantially larger than the latter. The discrepancies amount to 20 times for 10^{-1}M ice and even 200 times for 10^{-2}M ice. This is attributable to the simple assumption made above that the whole entrapped KCl solution contributes to the electrical conduction. Actually the brine distribution in ice is not simple, but the most portion of the solution may exist as isolated brine inclusions.

The large values of dielectric constant of KCl ice are considered to be produced by the migration and building up of mobile ions in the isolated brine inclusions. The dielectric properties of the heterogeneous or mixture dielectrics have been studied by MAXWELL (1892), WAGNER (1924) and others.
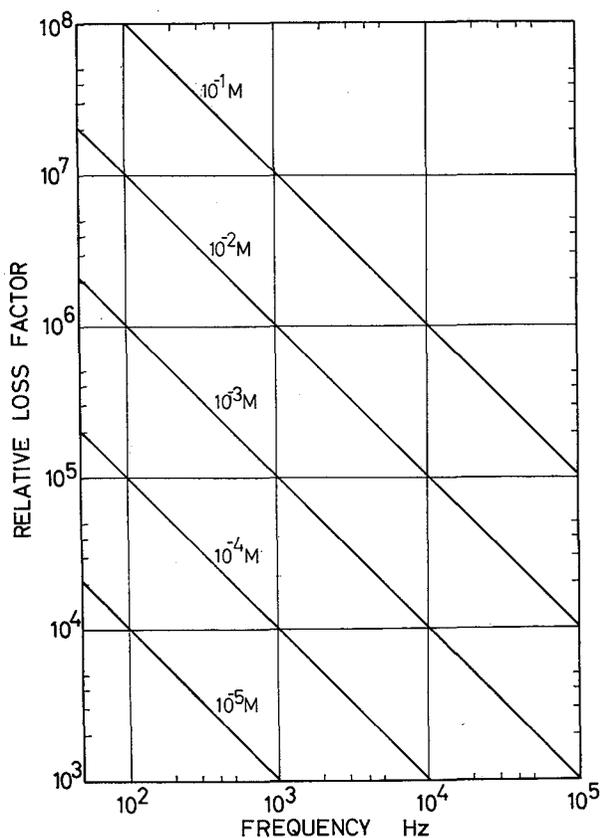
Fig. 6. Frequency dependence of the loss factor calculated by assuming that the whole KCl solution is responsible for the electric conduction. The temperature is −5°C and the parameter is the KCl concentration

The MAWELL-WAGNER-type polarization occurs due to the piling up of mobile charges at various boundaries between the components composing the system. When material 2 (dielectric constant and conductivity are κ_2 and σ_2, respectively) is dispersed in medium 1 (κ_1, σ_1) and the relation, $\kappa_1/\sigma_1 \neq \kappa_2/\sigma_2$, is satisfied, the charges will be piled up at the interfaces between materials 1 and 2 in an electric field, resulting in the so-called interfacial polarizations. Such interfacial polarizations depend upon the shape and the mode of distribution of the dipersoid as well as its volume fraction. According to Sillars' treatment (SILLARS 1937) in which the dipersoid is assumed to be ellipsoidal particles and oriented with their unique c-axes parallel to the applied electric field, the apparent dielectric constant and loss factor of

the mixture dielectric are given by

$$\kappa' = \kappa'_\infty + \frac{\kappa'_0 - \kappa'_\infty}{1 + \omega^2 \tau^2} \tag{II. 7}$$

and

$$\kappa'' = \frac{(\kappa'_0 - \kappa'_\infty)\,\omega\tau}{1 + \omega^2 \tau^2}\;, \tag{II. 8}$$

where κ'_∞ and κ'_0 are the limiting values of dielectric constant at $\omega \to \infty$ and $\omega \to 0$, respectively, and τ is the relaxation time. The forms of the equations are identical with those of Debye's equations with a single relaxation time, which have been derived for the molecular orientation in a homogeneous polar liquid (DEBYE 1929). κ'_∞, κ'_0 and τ are given by

$$\kappa'_\infty = \kappa_1 \left[1 + \frac{(\kappa_2 - \kappa_1)\,v}{\kappa_1 + A(\kappa_2 - \kappa_1)} \right], \tag{II. 9}$$

$$\kappa'_0 = \kappa_1 \left[1 + \frac{v}{A(1-v)} \right], \tag{II. 10}$$

and

$$\tau = \frac{\varepsilon}{A\sigma_2} \left[\kappa_1 + A(\kappa_2 - \kappa_1) \right], \tag{II. 11}$$

when $\sigma_1 \ll A\sigma_2$, where A is the depolarizing factor along the c-axis and depends upon the axial ratio, c/a, as follows

$$A = (a/c)^2 \left[\ln(2c/a) - 1 \right] \text{ when } c/a > 1\,,$$

$$A = 1/3 \text{ when } c/a = 1\,, \text{ and}$$

$$A \doteqdot 1 \text{ when } c/a < 1\,.$$

The loss factors of 10^{-1}M KCl ice at $-5°$C were calculated as functions of frequency and c/a, by using Eqs. II. 7–II. 11 and assuming that the whole KCl solution was dispersed in the forms of the ellipsoidal particles parallel to the field. The frequency dependence of the calculated loss factor is shown in Fig. 7. In the calculation, the following numerical values were used: the volume fraction of the KCl solution, $v = 0.0596$, the dielectric constant of pure ice at $-5°$C, $\kappa_1 = 73.6$, the dielectric constant of KCl solution in equilibrium at $-5°$C, $\kappa_2 = 63.5$, and its conductivity, $\sigma_2 = 9.4$ mho/m (LANDOLT-BÖRNSTEIN 1960). It was also assumed that no dielectric dispersions of the ice and KCl solution occurred in the frequency range considered in the calculation. In Fig. 7, the broken line, the envelope of curves
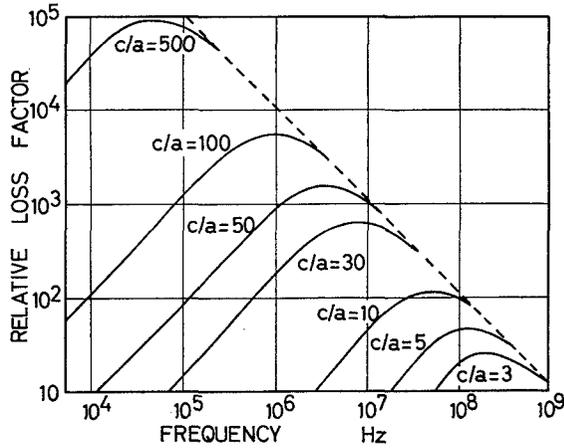
Fig. 7.   Frequency dependence of the loss factor for 0.1 M ice at −5°C, calculated from Eqs. II. 7–II. 11 for the axial ratio $c/a = 3 \sim 500$. The dashed line corresponds to Eq. II. 6

obtained for various values of c/a, is almost identical with uppermost straight line shown in Fig. 6. Therefore, if the loss factor of a given mixture dielectric is expressed by Eq. II. 6, it will give the maximum loss irrespective of the shape and distribution of the dispersoid. If we calculate the relaxation times of this KCl ice at −5°C, the values are extremely short, e. g. $\tau = 1.985 \times 10^{-10}$ s when $c/a = 1$, because the conductivity of KCl solution is very large. As seen in Fig. 7, the dielectric dispersion shifts toward the lower frequencies and the values of loss factor increase with the increasing axial ratio. The computed values of dielectric constant also increase, e. g., $\kappa_0' = 1.43 \times 10^3$ when $c/a = 30$, $\kappa_0' = 3.24 \times 10^3$ when $c/a = 50$, $\kappa_0' = 1.07 \times 10^4$ when $c/a = 100$ and $\kappa_0' = 1.98 \times 10^4$ when $c/a = 500$. Since the shape and the mode of the distribution of KCl solution are much complicated in the actual ice, measured dielectric properties are considered to be a superposition of contributions from the varieties of shapes and dimensions of the liquid inclusions. If we assume that the diameter of brine inclusion in KCl ice is 0.1 mm, the inclusions having the axial ratios of 100 and 500 may correspond to the lengths of 1 cm and 5 cm, respectively. Since the thickness of the specimen was less than about 1 cm in our measurement, it may be speculated that tiny inclusions might be connected in series in the ice. It was also confirmed that the measured values of dielectric constant and conductivity were not significantly altered by the perpendicular application of the field to the growth direction of the specimen, as has been reported on the natural sea ice (FUJINO 1967b). The following conclusion may be drawn:

the dielectric properties of KCl ice above its eutectic temperature are attributable to the interfacial polarization and the brine inclusions which are extremely irregular in shape and tortuous three-dimensionally.

The dielectric properties of KCl ice of the relatively lower KCl concentration are different from those of the higher concentration discussed above. When the KCl concentration was lower than about 5×10^{-3}M, sharp discontinuities at the eutectic temperature were not observed in the dielectric properties, which appeared in the higher concentration ice as shown in Fig. 3. This experimental fact may be explained as follows : the dielectric contributions of the phase change of the liquid inclusions are not significant because of their small volume fractions.

II. 4. *Dielectric properties of artificial mixture dielectrics*

The measurements discussed above have shown that the large values of dielectric constant and loss factor are originated by the liquid inclusions
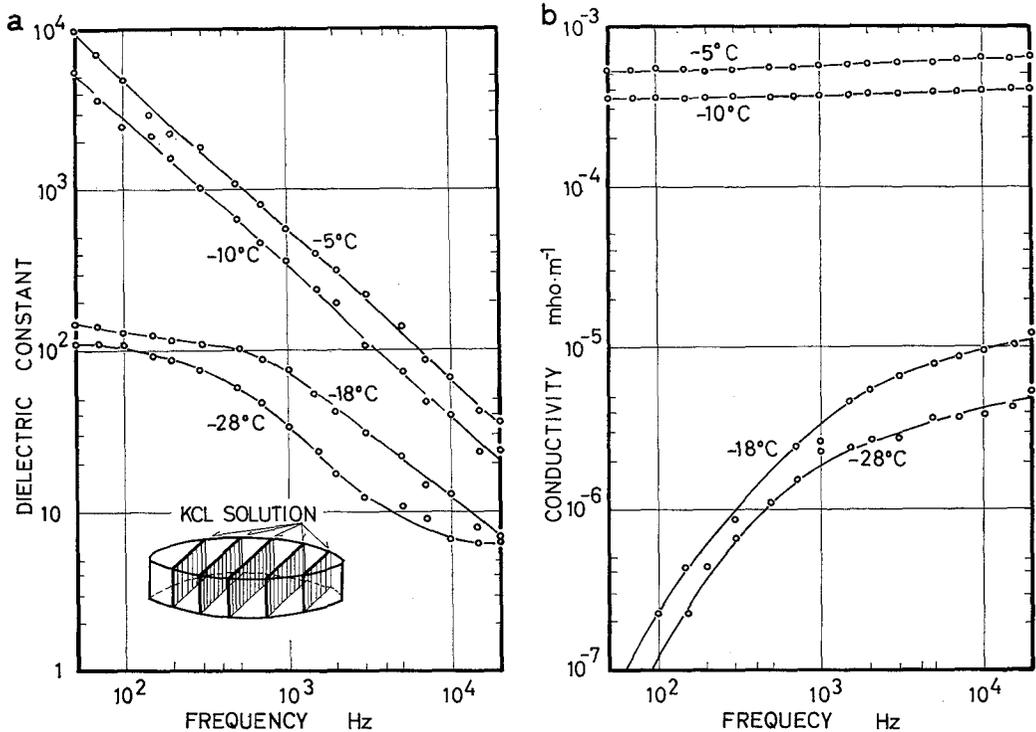

Fig. 8. Frequency dependedces of dielectric constant (a) and conductivity (b) of the artificial mixture ice containing KCl solution parallel to the electric field
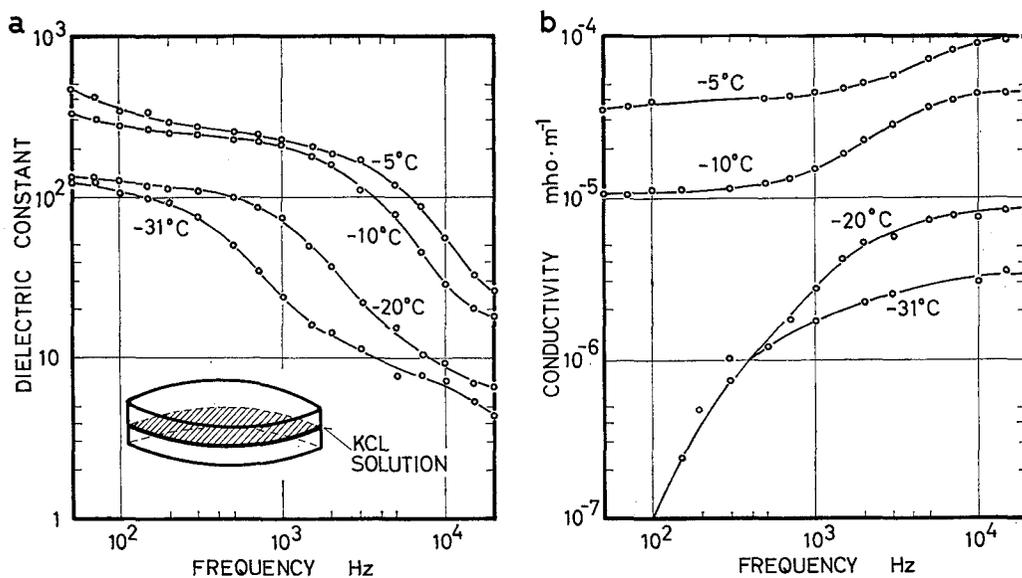
Fig. 9.   Frequency dependences of dielectric constant (a) and
conductivity (b) of the artificial mixture ice containing KCl
solution perpendicular to the electric field

contained in the irregular forms in the ice.   In order to ascertain this
conclusion the following experimentations were performed with artificial
dielectrics in which KCl solutions were distributed in a controlled manner :
     A circular plate of ice (1 cm in thickness) was prepared from pure ice
and five parallel cuts were engraved with a heated wire and then filled with
$0.5 \, cm^3$ of 3.0 M KCl solution.   Figure 8 shows the sketch of the specimen
thus made and its dielectric properties measured under the application of
an electric field parallel to the films of KCl solution.   Figure 9 shows the
sketch of another artificial dielectric.   In this specimen, a film of $0.5 \, cm^3$
of 3.0 M KCl solution was sandwiched between two pure ice slabs and the
field was imposed perpendicularly to the film.   As the apparent KCl con-
centration of the two specimens was approximately $3.6 \times 10^{-2} M$, the volume
fraction of the liquid solution was estimated as $v = 0.0230$ at $-5°C$ and
$v = 0.0116$ at $-10°C$.
     The dielectric properties were completely different from each other above
and below the eutectic temperature.   When the temperature was higher than
$-11°C$, the KCl solution provided effective electric conducting paths, but
the liquid films changed to the solid phase below the eutectic point (Fig. 8).
The frequency dependences shown in Fig. 8 are quite similar to those of

KCl ice grown by freezing the solution. In the case of Fig. 9, however, an increase in dielectric constant and conductivity was small compared with that of Fig. 8, and no linear relationship was found between $\ln \kappa'$ and $\ln f$ at temperatures above $-11°C$. These experimental results showed that the dielectric properties of KCl ice could be changed by the mode of distribution of KCl solution in ice.

II. 5. *Conclusions*

When the KCl concentration in ice was higher than about $5 \times 10^{-3} M$, large values of dielectric constant and loss factor were observed at temperatures above the eutectic point and at low frequencies. The values of dielectric constant and loss factor increased rapidly with increase in the temperature and KCl concentration, and the frequency dependence of loss factor approached to the relation, $\kappa'' \propto f^{-1}$. These dielectric properties could be explained by the MAXWELL-WAGNER-type interfacial polarization caused by the entrapped KCl liquid solutions in ice.

III. Dielectric properties of KCl ice below
the eutectic temperature

When the temperature is lower than the eutectic point, KCl ice can be considered to be a mixture dielectric composed of ice and solid KCl crystals. It may be expected that its dielectric properties might not be modified much by the existence of the solid inclusions of KCl since the KCl crystal is an electric insulator having a small value of dielectric constant, namely 4.7, and its volume fraction in ice is quite small, generally less than 0.01. However, as will be discussed in the following sections, the presence of a small quantity of KCl in ice produces significant alterations to the dielectric properties below the eutectic temperature.

III. 1. *Devices for measurements*

Figure 10 shows a photograph of a dielectric cell used in a dielectric measurement, which is made of chromium-plated brass and a Micalex sheet (K) and is approximately 3.4 kg in weight. The cell was composed of a center-electrode, a guard-ring-electrode (A), and a counter-electrode (C). The diameter of the center-electrode was 37.0 ± 0.1 mm and the inner diameter of the guard-ring-electrode was 39.0 ± 0.1 mm, making an air gap of 0.1 mm between them. The outer diameters of the guard-ring-electrode and the counter-electrode were both 49.0 mm. The cell constant was calculated by assuming that the effective diameter of the electrode was 38.0 mm.
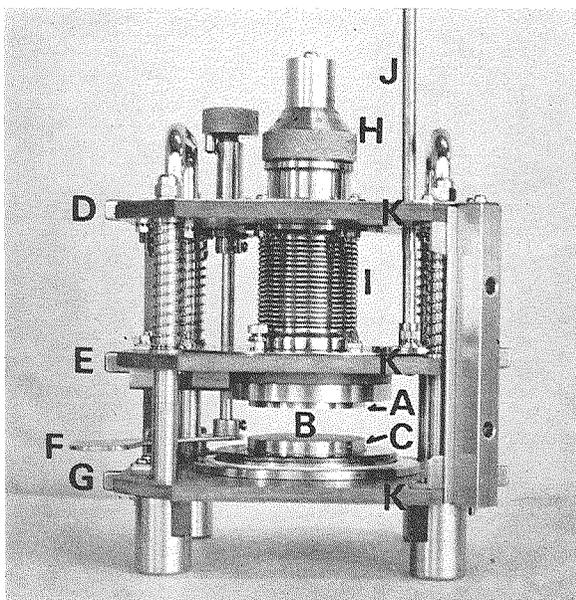
Fig. 10.   Photograph of a dielectric cell. A: guard-ring-electrode. The
      center-electrode is fixed inside of it. B: space between the electrodes
      in which an ice specimen is placed. C: counter-electrode, D, E and
      G: terminals of the guard-ring-, center-, and counter-electrode, respec-
      tively. F: electric shielding, H: microgauge, I: spring, J: platinum
      resistance thermometer, K: Micalex sheet

The close electrical contact between the specimen and the electrodes
was achieved by using the following two methods: thin gold foils were
adhered on the surfaces of the ice specimen in one method, and the speci-
men was frozen to the electrodes in the other.   An extremely thin, about
10 μm in thickness, gold foils of high quality was cut into discs of 37.0 mm
and 60 mm in diameter and adhered on the two surfaces of the ice specimen.
It was carefully placed in the space (B) between the electrodes and then the
upper electrodes were gently put down taking care not to make contact
between the center- and the guard-ring-electrode.   The latter method is
rather similar to that conducted in the preceding chapter.   A flat electric
heater (30 W) was inserted for about 5 minutes in the space, B, of the cell
maintained at $-30°$C.   When the surfaces of the electrodes became slightly
above 0°C, the ice specimen was inserted there.   Close contact was achieved
by the slight melting (less than 1 mm in thickness) and subsequent refreezing.
These two methods gave almost identical results in the dielectric measure-
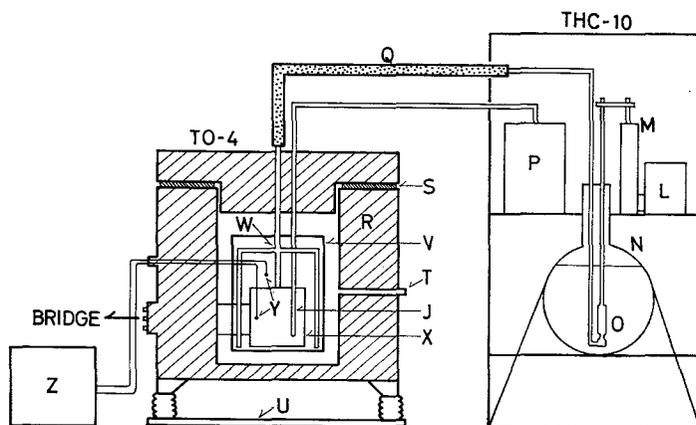ments, so that the latter was mainly employed in the measurements because

Fig. 11. Thermostat (TO–4) and the temperature-regulating system (THC–10).
L: motor, **M**: piston, **N**: bath of liquid N_2 (20 liters), **O**: pump, **P**: electronic
controlling system, **Q**: vacuum transferring tube, **R**: thermal insulation, **S**:
spacing, **T**: outlet for overflow, **U**: electric insulation, **V**: inner container, **W**:
four nozzles having numerous tiny holes, **X**: dielectric cell, **Y**: thermocouples,
Z: recorder, **J**: platinum resistance thermometer

of easier handling. The thickness of the specimen was measured in an
accuracy of 0.01 mm with a microgauge (H).

Main measurements were conducted at temperatures above −100°C,
but the temperature of the specimen could be cooled down to −180°C if
necessary. Figure 11 shows the schematic diagram of the cooling device
used. The diameter and depth of the inner container (V) of the thermostat
(TO–4) were 20 cm and 22 cm, respectively, in which liquid N_2 transported
from the regulating device (THC–10) with the pump (O) was spouted out
of numerous tiny holes cut on the four nozzles (W). The container was
accordingly filled with a fog of liquid N_2, in which the dielectric cell (X)
was placed. The flow rate of liquid N_2 was controlled automatically by
changing the speed of rotation of the driving motor (L) to maintain a given
temperature in an accuracy of ±0.3°C for many hours. Since the specimen
was in a close contact with the electrodes which had the high heat capacity
and thermal conductivity, it would be reasonable to assume that there are
no thermal gradients within the specimen. The temperature of the specimen
was measured with Cu–Co thermocouples (Y) of 0.2 mm in diameter which
were sealed in a protecting pipe (1 mm in diameter) containing magnesium
oxide.

Dielectric measurements were conducted after the specimen was main-
tained at a desired temperature for at least 1.5 hours. The fracture of the
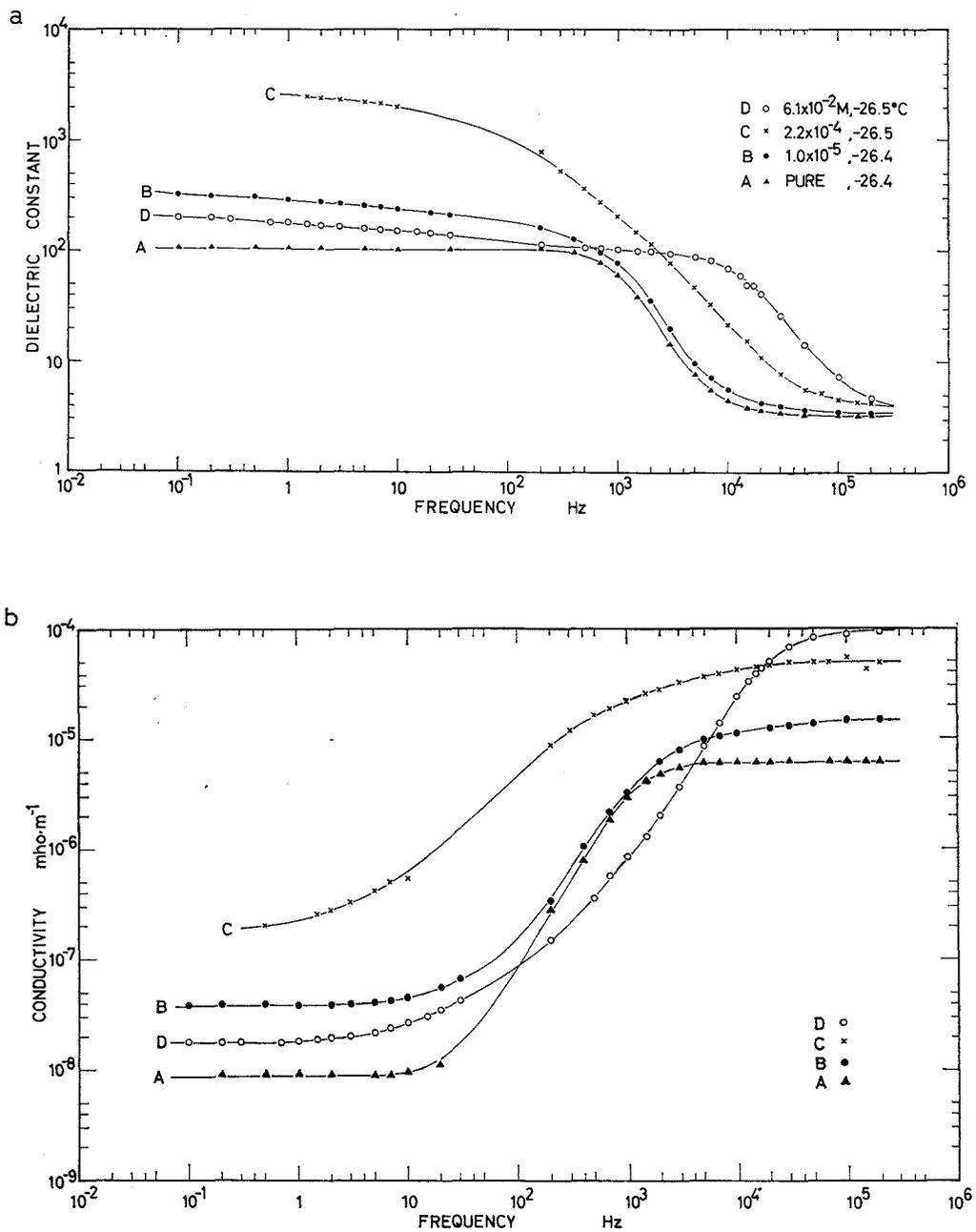
a

b

Fig. 12.   Typical frequency dependences of dielectric constant (a) and
conductivity (b) for KCl ice below the eutectic temperature

ice specimen and the failure of the close contact with the electrodes might
be anticipated in case of rapid change of temperature, but they seldom
occurred in our measurements.   The KCl concentration of the specimen
was determined by measuring the electrical conductivity of the melted ice
after each dielectric measurement was completed.   The electrical conduc-
tivity was measured at $+25°C$ by using Toa Dempa CB–1D and CM–2A
conductometers.

The dielectric measurements were carried out in a frequency range from
0.1 Hz to 2×10^5 Hz by using Ando Denki TR–4 and TR–10C bridges.

III. 2.   *Concentration dependence and classification of KCl ice*

No liquid inclusions can exist in KCl ice at temperatures below the
eutectic point, but the concentration dependence of the dielectric properties
was very complicated.   Figure 12 displays the frequency dependences of
dielectric constant (a) and conductivity (b) measured at $-26.5°C$ for the
typical KCl ices of three concentrations, i. e., 1.0×10^{-5}M (curves B), 2.2×10^{-4}M (C) and 6.1×10^{-2}M (D).   Curves A are those for pure ice.   The
dielectric properties of pure ice show the typical Debye dispersion in a fre-
quency range from 10^2Hz to 10^4Hz, which is originated by the orientational
polarization of H_2O molecules and can precisely be represented by Eqs. II.7
and II. 8.   However, the range of curves B, C and D shifted toward higher
frequencies as the concentration was increased.   It should be noted that,
though the concentration of specimen D is higher than those of B and C,
the value of its dielectric constant is smaller than those of B and C at low
frequencies.

These complicated concentration dependences can be illustrated more
clearly in Fig. 13, in which the dielectric constant (a) and loss factor (b)
measured at $-20°C$ were plotted as a function of KCl concentration.   The
parameter is the frequency.   For the frequency of 10^2Hz, the dielectric
constant has a maximum value around 10^{-3}M, but begins to show several
maxima and minima as the frequency becomes higher.   When the KCl
concentration is higher than about 10^{-2}M the dispersion becomes small and
the dielectric constant tends to decrease with a further increase in the con-
centration.   Thus the dielectric properties of KCl ice below the eutectic
temperature seem to be different from each other above and below the KCl
concentration of 10^{-2}M.   In addition to this, the macroscopic grain texture
of KCl ice was also observed to change around this concentration range.
For the sake of covenience, KCl ice will be classified henceforth into two
types, "high-concentration ice" and "low-concentration ice", with 10^{-2}M as
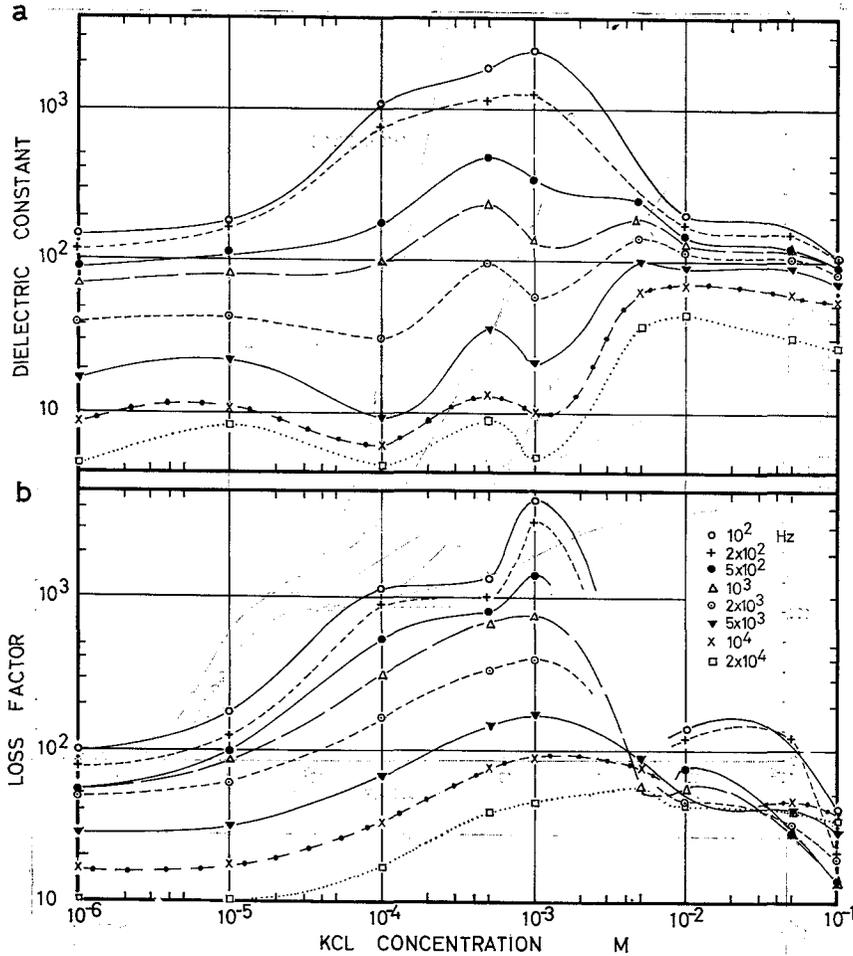the critical concentration.

Fig. 13. Concentration dependences of dielectric constant
(a) and loss factor (b). The temperature is −20°C and the
parameter is the frequency

III. 3. *Dielectric properties of the high-concentration KCl ice*

Figure 14 shows the frequency dependences of dielectric constant (a) and conductivity (b) of the high-concentration ice measured at a temperature around −36°C. Dotted lines refer to specimen 17 which belongs to the low-concentration ice. It will be seen that the values of dielectric constant of the high-concentration ices at low frequencies are not simply proportional to the KCl content in ice. A general aspect of the dispersion shows several inflections and plateaus, suggesting that different relaxation mechanisms must
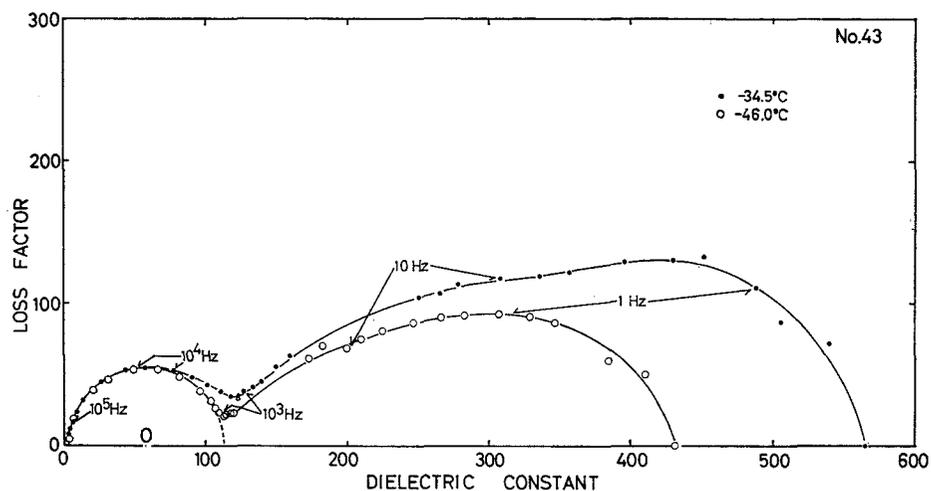
a

b
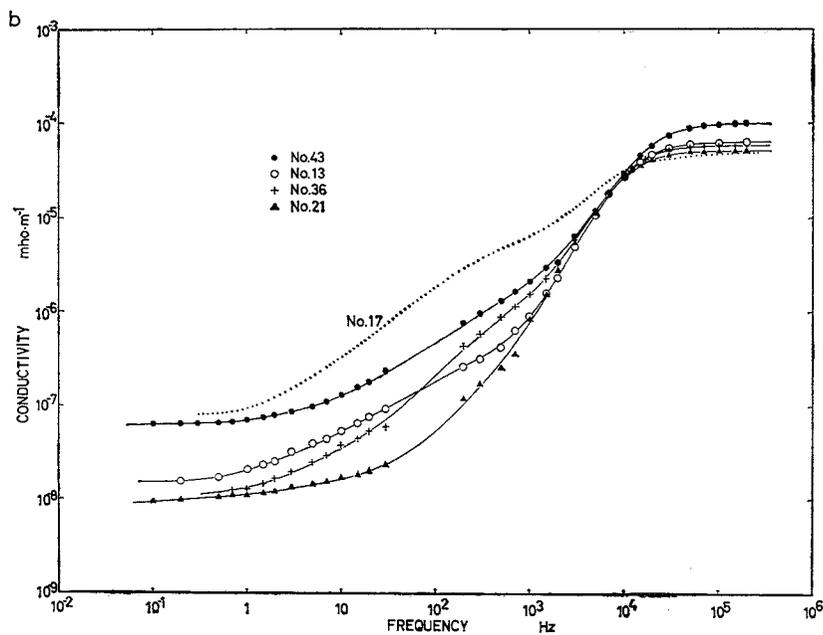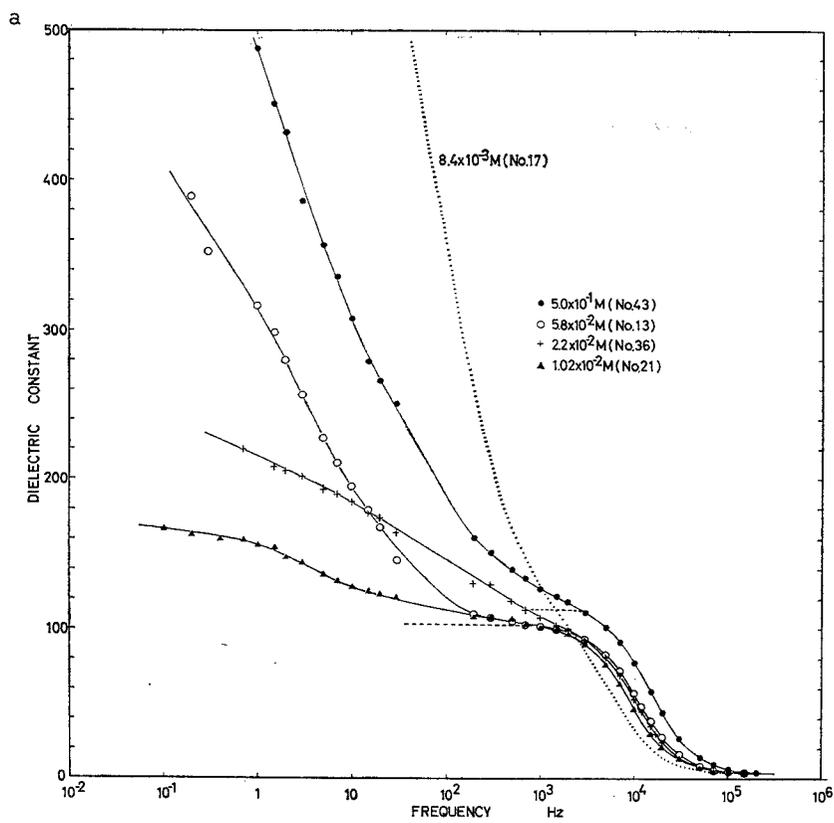
Fig. 15.   Cole-Cole diagram of the high-concentration KCl ice (0.5 M)

be taking place.   A similar behaviour can be seen in the conductivity in Fig. 14. b.

In order to separate the primary polarization mechanism from others, the dielectric constant and loss factor were plotted in a complex plane. Figure 15 shows the so-called Cole-Cole diagram of specimen 43 containing 0.5 M of KCl.   In this plot, the dielectric loss due to the d. c. conduction was subtracted from the observed loss factor by using the low-frequency conductivity obtained by extrapolation.   It can be seen that there are two different dielectric dispersions in the complex dielectric constant.   The values of the complex dielectric constant at high frequencies delineated a well defined semicircle (indicated by a dashed curve), the center of which lay almost exactly on the κ'-axis, implying that the dielectric dispersion occurring in this region could be described by the single relaxation mechanism expressed by Debye's equations, Eqs. II. 7. and II. 8.   On the other hand, the Cole-Cole diagram of the dielectric dispersion appearing at lower frequencies was not a simple semicircle but similar to the locus represented by the lemniscate rule (THE PHYS. SOC. JAPAN 1963), which is written

$$\kappa^* = \kappa'_\infty + \frac{\kappa'_0 - \kappa'_\infty}{(1 + i\omega\tau)^\beta} , \tag{III. 1}$$

Fig. 14.   Frequency dependences of dielectric constant (a) and conductivity (b).   The exact temperatures are as follows: No. 13 (−35.8°C), No. 21 (−36.5°C), No. 36 (−35.8°C) and No. 43 (−34.5°C).   The dotted lines (No. 17) show the frequency dependences of a low-concentration ice (8.4×10⁻³ M, −35.8°C)
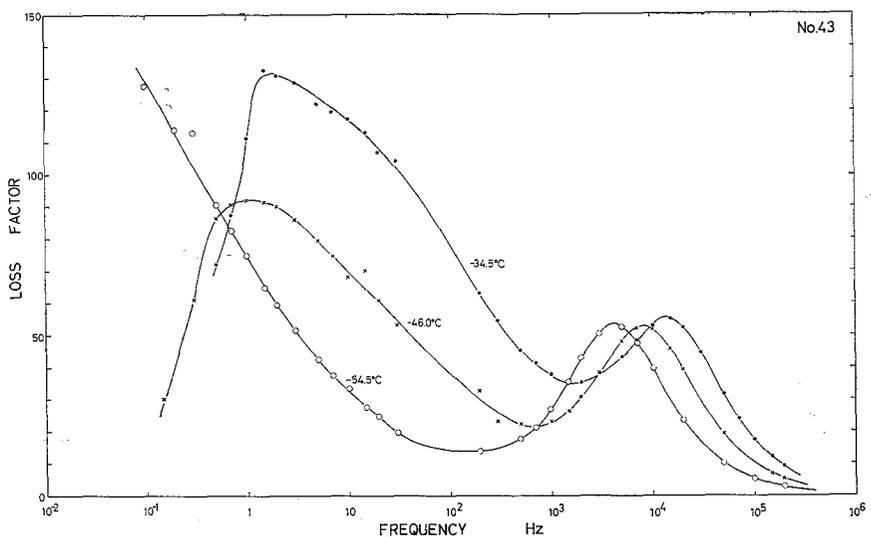
Fig. 16.   Frequency dependence of loss factor of the
high-concentration KCl ice (0.5 M)

where β is a numerical constant $(0 \leq \beta \leq 1)$.   When $\beta = 1$ this equation corresponds to Debye's equations, and when $\beta = 0.5$, it makes a locus which is generally called Bernoulli's lemniscate.   The lemniscate rule has been found to describe favourably the complex dielectric constants of glycerine (DAVIDSON and COLE 1950) and other chain polymers such as polyvinyl acetate (MEAD and FUOSS 1941), all of which have the relaxation times distributed in a relatively wide range.   Therefore, it can be concluded that the dielectric dispersion observed in a low frequency range may be composed of several relaxation mechanisms.

Figure 16 shows the frequency dependence of loss factor, which was obtained also by subtracting the d. c. losses from the observed values for the same specimen.   The well defined bell-shaped peaks appearing around 10^4 Hz showed a tendency to shift toward higher frequencies as the temperature was raised.   Usually the relaxation time for the dielectric dispersion is calculated from the frequency at which the dielectric loss factor has a maximum, but precise determinations cannot be made by such a method, because contributions from the dispersion at lower frequencies are effectively superimposed on that at high frequencies.   As the high frequency dispersion of this specimen can be described by Debye's equations, the relaxation time may be calculated as follows: if we rewrite Debye's equations in the forms of
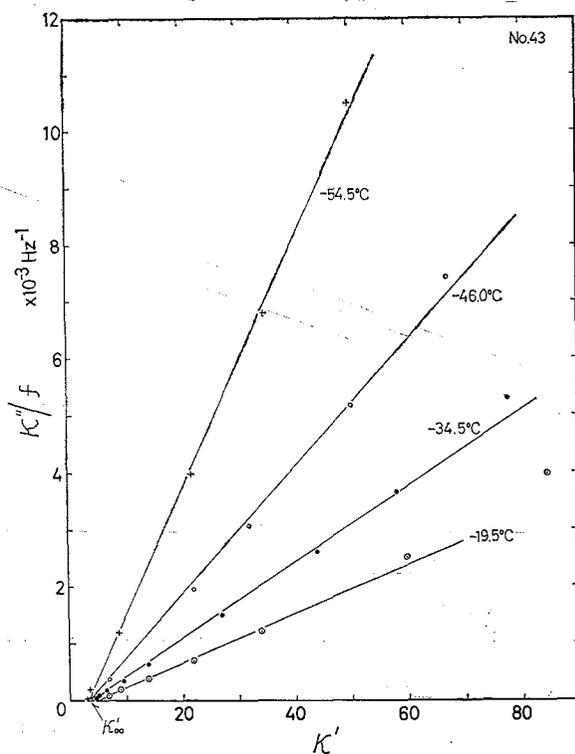
Fig. 17. Relation between κ''/f and κ'

$$\kappa' - \kappa'_\infty = \frac{1}{\tau} \cdot \frac{\kappa''}{\omega} \qquad \qquad \text{(III. 2)}$$

and

$$\kappa'_0 - \kappa' = \tau \cdot (\kappa''\omega), \qquad \qquad \text{(III. 3)}$$

the relations between κ' and κ''/ω or $\kappa''\omega$ can be expressed by a straight line. Figure 17 shows the plot of κ' and κ''/f for the same specimen as above. Since lineality was satisfied up to $\kappa' \fallingdotseq 70$, the relaxation times at different temperatures could be estimated from the slopes of straight lines, which were plotted in Fig. 18 against the reciprocal of the absolute temperature. In the figure the relaxation times of three other specimens were also plotted. From these, the average activation energy was found to be 5.3 kcal/mol. The activation energy obtained in the same way for pure ice was 13.5 kcal/mol, which is nearly two times larger than that obtained for the high-frequency dispersion. It has been reported that the apparent
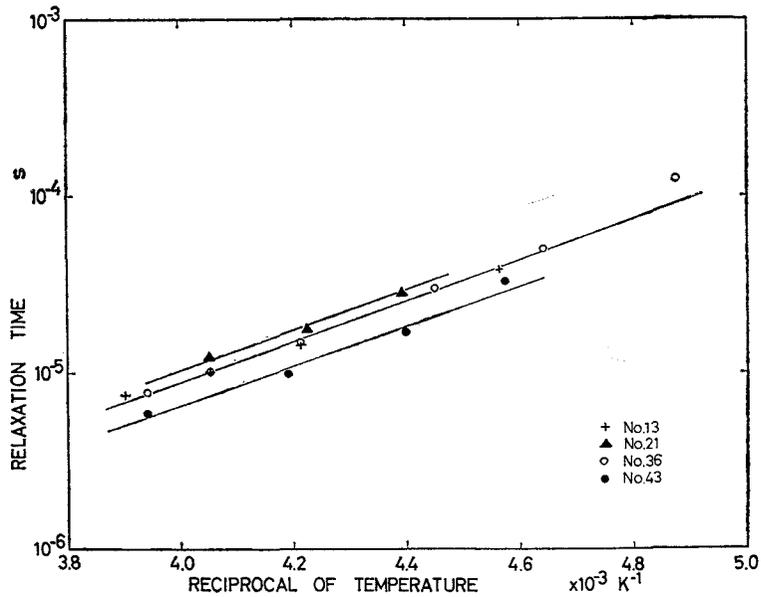
Fig. 18.   Plot of the dielectric relaxation time against the reciprocal
of the absolute temperature.   The activation energy is 5.3 kca/mol

activation energy of the dielectric dispersion of sea ice observed at tem-
peratures below its eutectic point showed the lower value similar to ours
(approximately 6.3 kcal/mol, Fujino 1967b).   It is obvious that the decrease
in the activation energy is caused by the impurities entrapped in ice, but
the detailed mechanisms have not been understood.

III. 4.   Dielectric properties of the low-concentration KCl ice

As seen in Fig. 13, the frequency dependences of the dielectric properties
of ice containing KCl less than 10^{-2}M showed a much more complicated
behaviour compared with those of the high-concentration ice.   Figures 19. a
and 19. b show the frequency dependences of dielectric constant and con-
ductivity of the low-concentration KCl ice as functions of the concentration.
Dotted lines indicate the values of pure ice.   The addition of a small amount
of KCl gave rise to a significant increase in dielectric constant even at tem-
peratures lower than the eutectic point.   The concentration of 10^{-5}M, for
instance, means that only one KCl molecule exists within 5.6×10^6 molecules
of H_2O.   In the case of such low concentration ice, the proportionality of
dielectric constant and conductivity to the KCl concentration was not ob-
served.   Note curves D indicated by broken lines in Fig. 19.   This specimen
contained 2.65×10^{-5}M of KCl, but its value of dielectric constant was
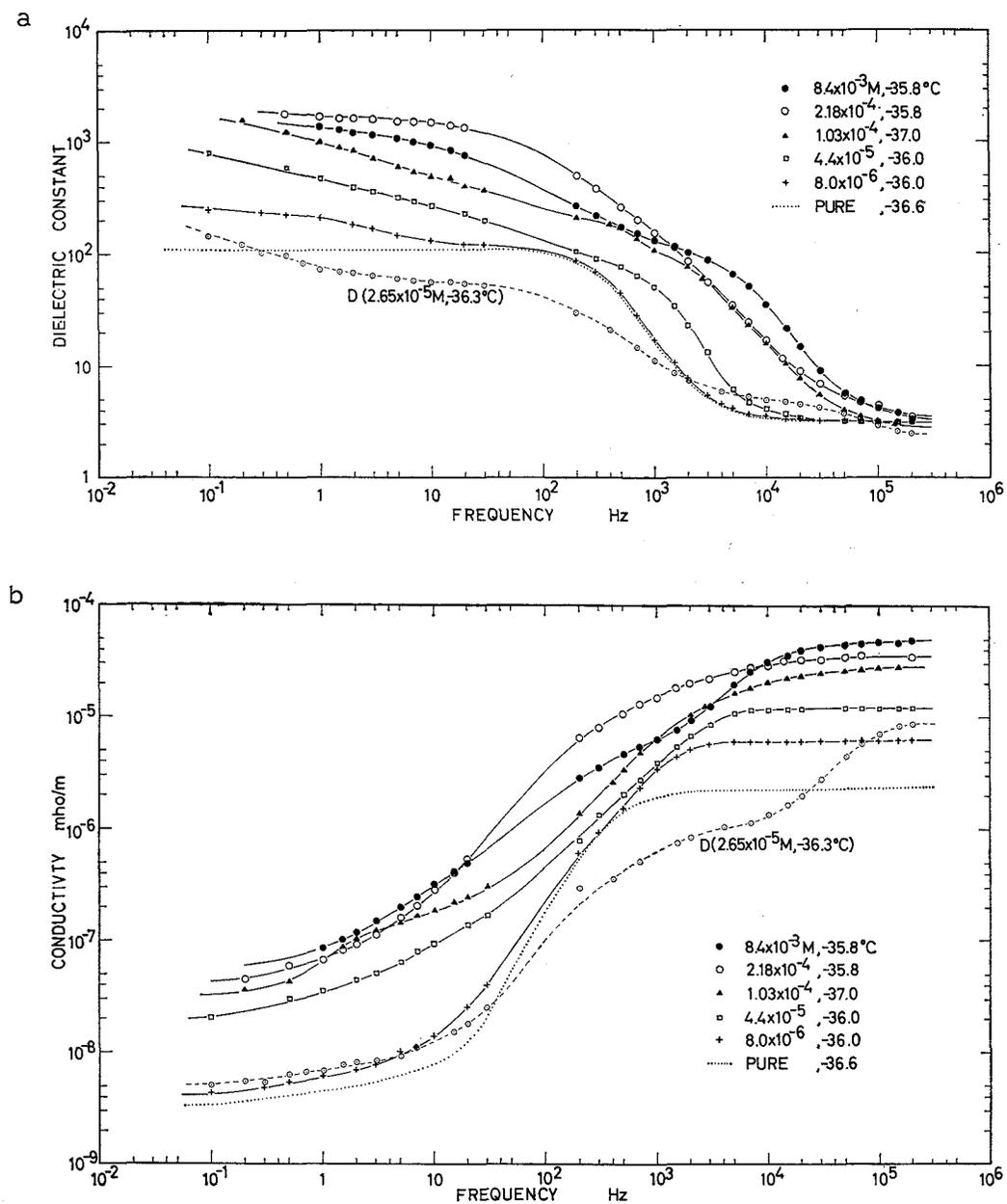
a

b

Fig. 19. Frequency dependences of dielectric constant
(a) and conductivity (b) of the low-concentration KCl
ice. The parameter is the KCl concentration

considerably smaller than that of pure ice. Careful crystallographic inspections revealed that this specimen was composed of only 2 or 3 grains although other specimens contained more than 20 grains. Therefore, specimen D contains only a few grain boundaries where the solutes are mostly segregated. From the experimental result that the considerable reduction of the dielectric constant occurred in specimen D and the fact that the value of dielectric constant of pure polycrystalline ice is nearly the same as that of pure monocrystalline ice, the following inference may be drawn : if KCl molecules are contained in a single crystal of ice in the from of solid solution, the apparent dielectric constant may be reduced. Detailed discussion of this problem will be presented in Chapter IV.

From the results shown in Fig. 19, it becomes important to examine the grain size dependence of the dielectric constant of KCl ice. Before discussing this experiment it must be necessary to test whether the dielectric polarization is caused either by the effect occurring near the interfaces between the specimen and the electrodes or by that occurring in the bulk of the specimen. Figure 20 gives a relation between the product of the measured capacitance and the thickness, $C_x \cdot d$, and the thickness, d, of the specimen. As seen in this figure the product can be regarded as a constant, implying that the dielectric constant computed from the capacitance is independent of the thickness of the specimen. Similar results were obtained by
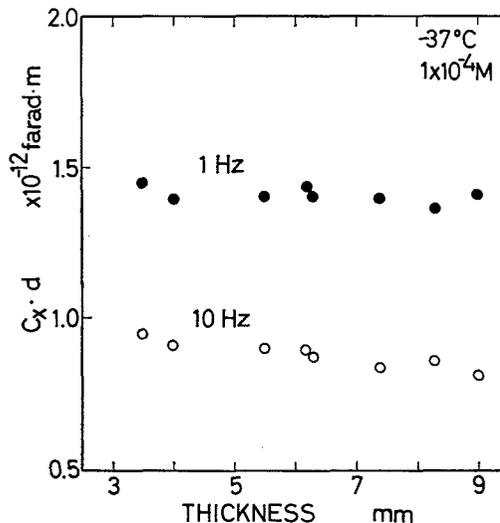

Fig. 20. Relation between the product of capacitance and thickness ($c_x \cdot d$) and the thickness (d) of the specimen

measurements at other temperatures and concentrations, and also for the conductance.

Since the low-concentration ice in point is polycrystalline composed of many grains in which most of KCl is considered to be entrapped at grain boundaries, the conclusion obtained above suggests that polarizations are mainly taking place near the grain boundaries. Figure 21 shows the grain size dependence of dielectric constant measured at 1 Hz. In this experiment, the grain size of a specimen was changed between 2~8 mm in the average diameter. As seen in this figure, the dielectric constant was almost independent of the grain size, but only dependent upon the KCl concentration. A similar trend was observed at other frequencies, and the conductivity did not depend upon the grain size either. As the diameter of the electrode used was 37.0 mm, the numbers of grains in the specimen can be roughly estimated as 160 and 20 for the average grain sizes of 3 mm and 8 mm, respectively. Therefore, the experimental result suggests that if the specimen consists of more than about 20 grains at least, the grain boundaries
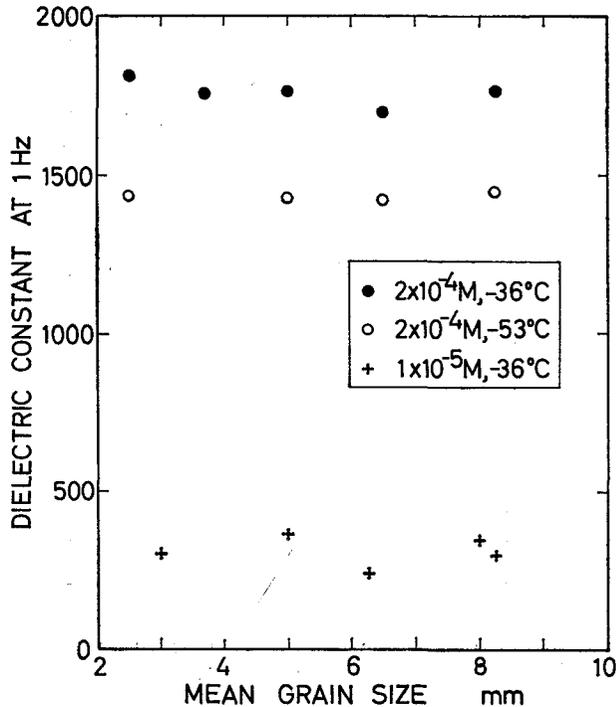

Fig. 21.   Relation between the dielectric constant at 1 Hz
and the mean size of grains composing a specimen

contained can afford sufficient microscopic discontinuities enough to produce the large values and dispersion of dielectric constant as observed in the measurements. However, if the number of grains in the specimen is reduced to 2 or 3, contributions from the grain boundaries diminish and other mechanisms occurring within the grains become predominant, which is the case shown by specimen D in Fig. 19. As will be discussed in Chapter IV, a single crystal of ice grown from dilute KCl solution incorporates chlorine ions preferentially in the crystal lattice, and consequently a significant reduction of the dielectric constant occurs. This situation should also be taking place within individual grains in the polycrystalline KCl ice. However, our experimentation suggests that if the number of grains in the specimen exceeds 20 at least, the effect reducing the dielectric constant due to the chlorine incorporation must be masked by contributions from the impurities segregated at the grain boundaries.
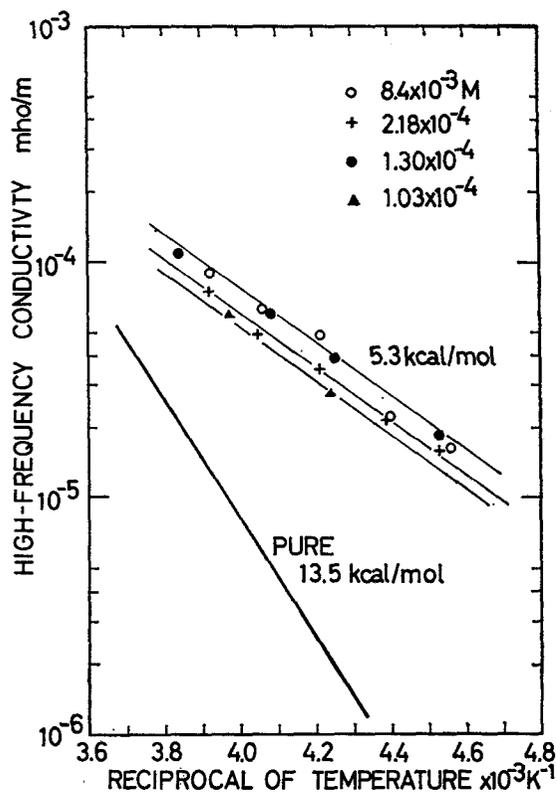

Fig. 22. Plot of the limiting high-frequency conductivity
against the reciprocal of the absolute temperature

In Figs. 22 and 23, the limiting high-frequency and low-frequency conductivities of the low-concentration KCl ice were plotted against the inverse absolute temperature. The limiting high-frequency conductivity includes both the effects taking place within grains and at grain boundaries. The activation energy calculated from the slopes of straight lines in Fig. 22 was found to be 5.3 kcal/mol. This value is significantly different from that of pure polycrystalline ice (13.5 kcal/mol), but that of the chlorine-doped single crystal of ice is 5.76 kcal/mol as will be seen in Chapter IV. The coincidence of the two energies suggests that the dielectric properties of the individual grains which constitute the polycrystalline ice have been modified to a large extent by the probable incorporation of chlorine. The apparent activation energy of the limiting low-frequency conductivity in Fig. 23 is 17.5 kcal/mol, which is somewhat larger as compared with that of pure ice (12.3 kcal/mol, BRADLEY 1957). The author believes that the deviation has come from the
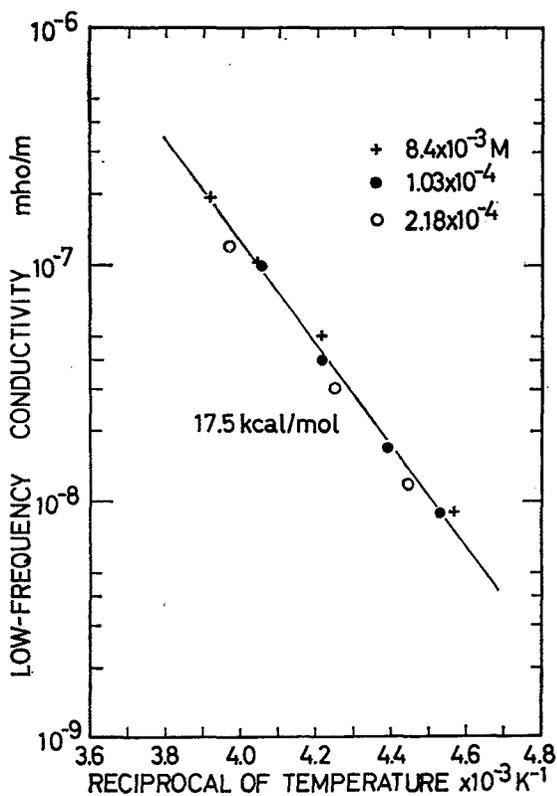

Fig. 23. Plot of the limiting low-frequency conductivity against the reciprocal of the absolute temperature

alteration of the conduction mechanism in the ice, i.e. the predominant effect of the d.c. conduction along the grain boundaries, because it has been reported that the activation energy associated with the d.c. conduction along ice surfaces and interfaces is considerably larger than that for the conduction within the bulk, namely 30~35 kcal/mol (BULLEMER and RIEHL 1966, MAENO 1972). On the other hand, it will be shown in the next chapter that the values of the low-frequency conductivity of monocrystalline ice are considerably increased by the chlorine incorporation in the crystal lattice, the increase amounting to the conductivity of polycrystalline KCl ice. A similar increase might be expected in each of the grains composing the specimens of Fig. 23, but the observed values are decreasing rapidly as the temperature is lowered. To this point, the following speculative explanation could be made : the grain boundaries, especially those containing some impurities, provide effective paths for d.c. conduction at relatively high temperatures, but they rapidly change to non-conductive barriers for the conduction as the temperature is lowered, since the activation energy for surface conduction is extremely large; this may lead to the observed result that the low-frequency conductivity of polycrystalline KCl ice is even lower than that of the chlorine-doped single crystal of ice, especially at lower temperatures.

SMYTH and HITCHOCK (1932) reported that the dielectric properties of ice were enormously modified by a slight addition of KCl. They measured the dielectric constants of ice grown from the KCl solution of 2×10^{-4} M in a frequency range from 3×10^2 Hz to 6×10^4 Hz and found that the value of dielectric constant was larger than that of pure ice, though they did not report the actual concentration of the specimen used. One of the notable findings in their experiment was the thermal hysteresis of dielectric constant : the values measured on cooling down and warming up were not identical. This hysteresis phenomenon suggests that a long time is required to attain a thermal equilibrium in the KCl ice. In our experiment, such a hysteresis was not observed because every measurement was made after the specimen was maintained at a given temperature for 1.5 hours at least.

III. 5. *Conclusions*

When the temperature of polycrystalline KCl ice is lower than the eutectic point, the KCl impurity segregated at grain boundaries changes to solid particles. If we assume that the KCl ice is a heterogeneous dielectric in which solid KCl particles are dispersed uniformly in pure ice, its dielectric properties may not be very different from those of pure polycrystalline ice because of the small volume fraction and high electrical resistivity of the

dispersoid. However, the values of dielectric constant and loss factor increased enormously with the addition of a small quantity of KCl. The increase was rather predominant at lower frequencies and extended toward higher frequencies as the concentration was raised. The rate of increase of dielectric constant was not always proportional to the concentration.

In the high-concentration KCl ice ($>10^{-2}$M), two kinds of dielectric dispersions were observed separately in different frequency ranges. One of the dispersions was found at frequencies much higher than those of pure ice, and the value of activation energy for the relaxation was calculated as 5.3 kcal/mol assuming that a single relaxation mechanism was responsible for it. The other dispersion was observed at much lower frequencies, suggesting that it may be caused by several complicated polarization mechanisms.

In the low-concentration KCl ice ($<10^{-2}$M), the significant modifications of dielectric dispersion were observed in a wide frequency range. It was found that the values of dielectric constant did not depend upon the thickness of a specimen and the average size of grains.

IV. Dielectric properties of single crystals of chlorine-doped ice

As shown in Fig. 19 in Chapter III, the specimen composed of a few grains exhibited the small values of dielectric constant compared with those of pure ice. This result suggests that the dielectric properties of a single crystal of ice grown from KCl solution might be considerably different from those of polycrystalline ice. As a single crystal does not contain any macroscopic grain boundaries the KCl impurity should be incorporated in the crystal lattice of ice. The purpose of this chapter is to clarify how the dielectric properties of the single crystal of ice are modified by the incorporation of the solute.

IV. 1. *Growth of single crystals of ice from KCl solution and distribution coefficients of potassium and chlorine*

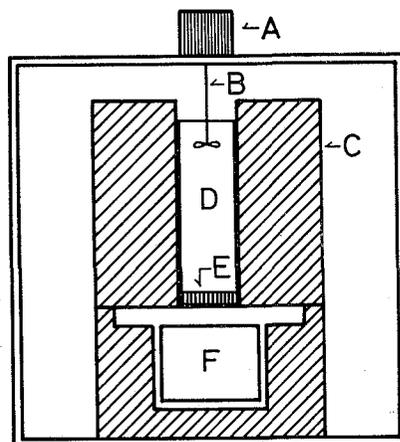Figure 24 shows schematically a device for growing single crystal of ice.

Fig. 24. Device for growing a single crystals of ice from KCl solution. **A**: motor, **B**: stirrer, **C**: thermal insulation, **D**: container of KCl solution, **E**: seed crystal, **F**: cold box filled with crushed solid CO_2

D is a thermally insulated Plexiglas container (6.5 cm in diameter and 20 cm in depth) of KCl solution. A seed crystal, E, was attached to the bottom of the container. When the container was placed on a cold box, F, filled with crushed solid CO_2, crystallization started from the bottom. The rate of freezing was 1.5 to 2.5 μm/s, and the solution was gently stirred (B, 60 r.p.m.) to prevent the accumulation of rejected solutes near the interface. The seed
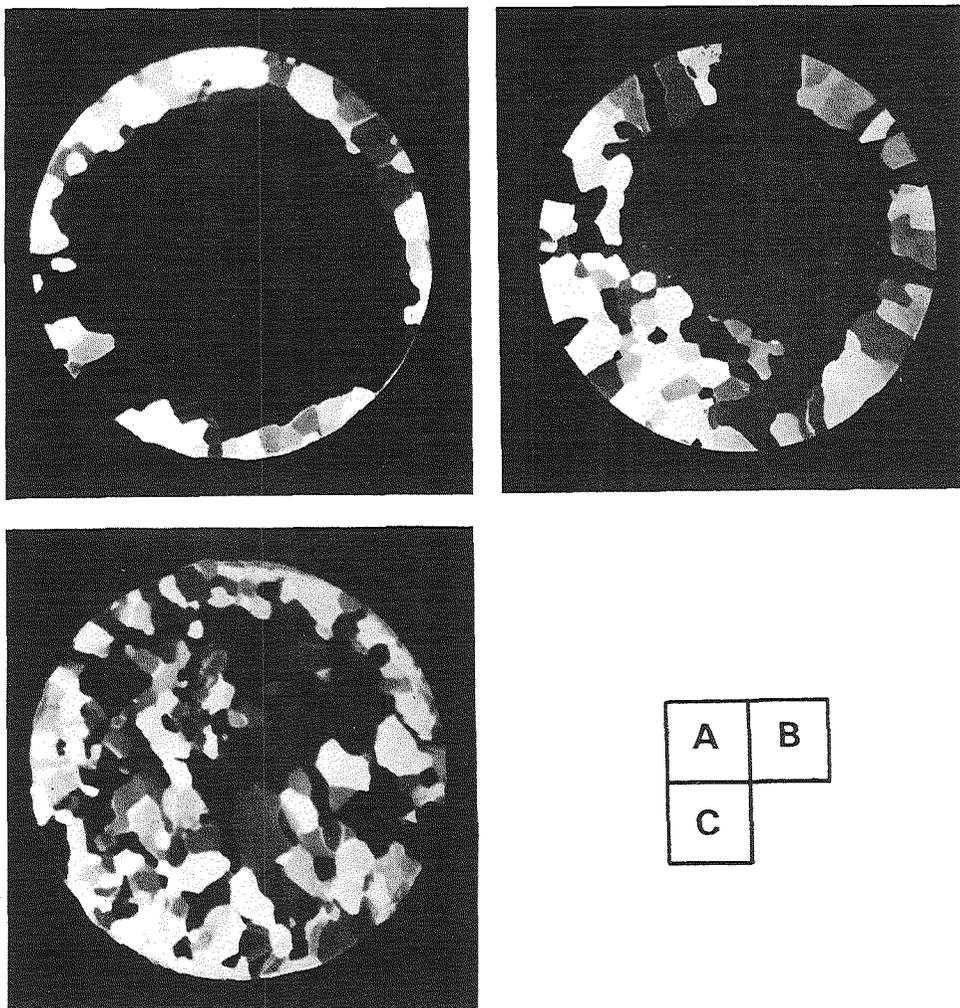

Fig. 25. Photographs of the horizontal cross sections of ice grown from KCl solution, taken under crossed polarized light. A: ice grown from the 1.19×10^{-5} M solution, B: ice grown from the 1.29×10^{-4} M solution, C: ice grown from the 1.40×10^{-2} M solution. Magnification $\times 0.85$

crystal was prepared from a large single crystal of ice obtained from the Mendenhall Glacier in Alaska, in a way in which its c-axis was parallel to the direction of freezing.

Figure 25 displays the photographs, taken under polarized light, of the horizontal cross sections of ice grown. In our device, many small grains having different crystallographic orientations developed from the side wall of the container, but when the KCl concentration of the mother solution was low the growth of a single crystal of ice as large as 5 cm in diameter was possible as shown by A. The growth of small grains at the peripheries became more frequent as the concentration increased, by which the development of the single crystal was disturbed as shown by B and C. Specimens for chemical and electrical measurements were cut out carefully from the central monocrystalline portion of the ice.

The concentrations of potassium and chlorine ions in the single crystal of ice were measured separately by using the ion-selective-electrodes, namely a Corning liquid-ion-exchange-potassium electrode and a Corning chloride-solid-state electrode, after the specimen was permitted to melt. Figure 26 shows the apparent distribution coefficients plotted against the KCl concentration of the mother solution. The apparent distribution coefficients of the cation and anion are defined as $K_{K^+}=C_{K^+}/C_{KCl}$ and $K_{Cl^-}=C_{Cl^-}/C_{KCl}$, where C_{K^+} and C_{Cl^-} are respectively the concentrations of potassium and chlorine in the single crystal of ice and C_{KCl} is the KCl concentration of the mother
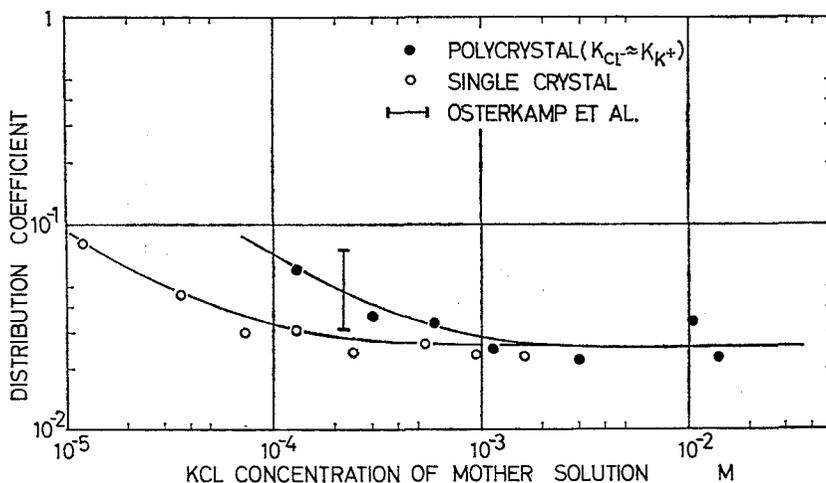

Fig. 26. Distribution coefficients of chlorine (○) for the monocrystalline growth and potassium chloride (●) for the polycrystalline growth, versus the KCl concentration of the mother solution
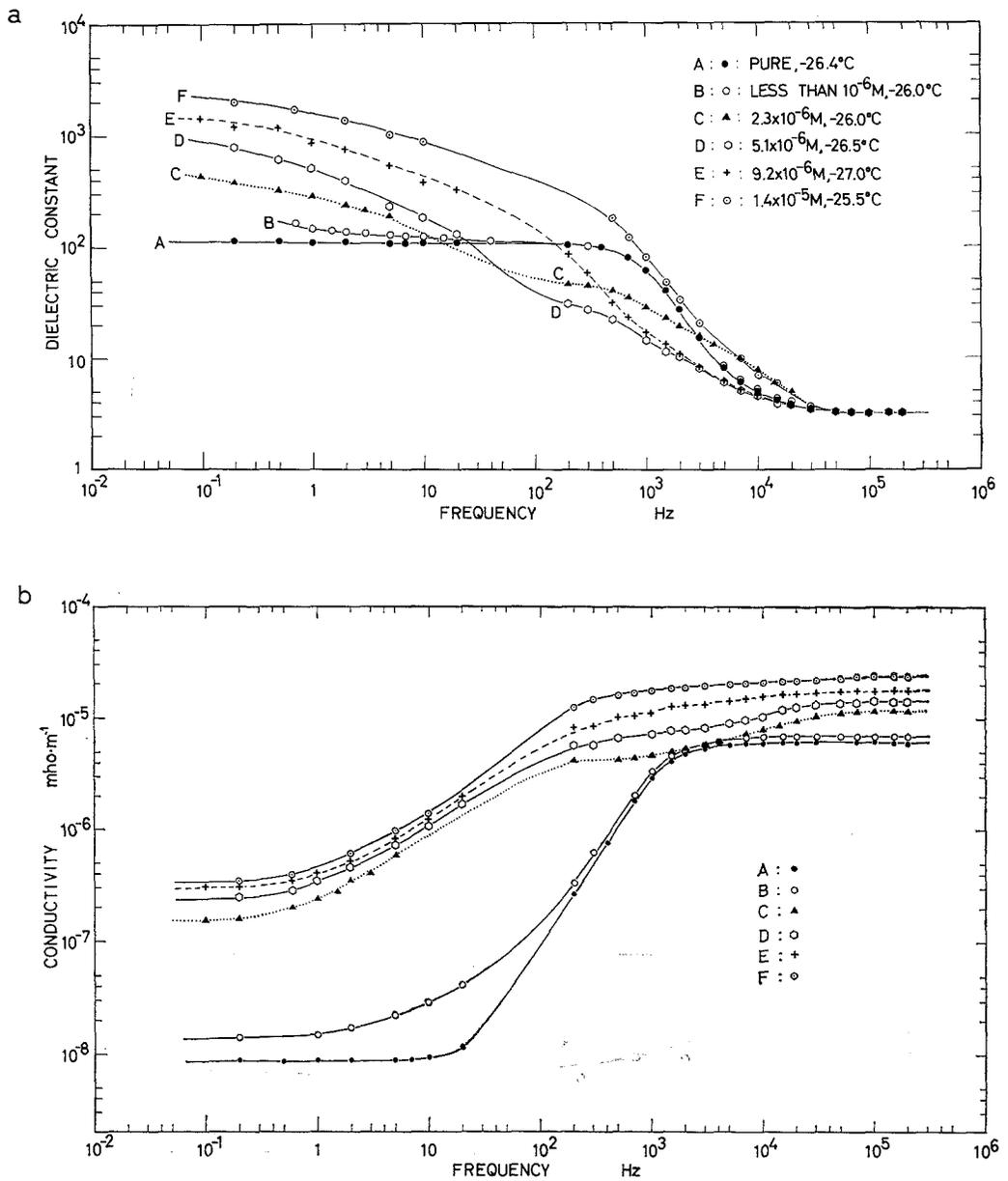
a

b

Fig. 27. Frequency dependences of dielectric constant
(a) and conductivity (b) of single crystals of ice con-
taining different amounts of chlorine

solution.   It was found that the chlorine ions were only preferentially incorporated in the single crystal of ice, but the equal amounts of the cation and anion were found in the polycrystalline ice, which was formed when the KCl concentration was higher than about 3×10^{-3}M.   The range of the distribution coefficient obtained by OSTERKAMP and WEBER (1970) is shown in the figure.   They observed a freezing potential as high as 10 volts between the KCl solution and the developing ice.   This seems to be prominent evidence showing the charge separation at the interface and the preferential incorporation of chlorine into ice.   In our experiment, the upper limit of the chlorine incorporation in the single crystal of ice was about 1×10^{-4}M.   This value is very close to that obtained for the HCl incorporation in a single crystal of ice, 2×10^{-4}M (SEIDENSTICKER 1972).

IV. 2. *Dielectric properties of single crystals of ice containing chlorine*

It has been reported that the dielectric constant of a single crystal of pure ice measured by the application of the electric field parallel to the c-axis of the specimen is larger by about 12 per cent $(-20°C)$ compared with that perpendicular to the c-axis (HUMBEL *et al.* 1953).   Such an anisotropy, however, was not observed in the chlorine-doped crystals grown in our device, so that the main measurements were carried out by the parallel application of the field to the c-axis of the specimen.   Figure 27 shows the frequency dependences of dielectric constant and conductivity measured at a temperature around $-26°C$ for five single crystals of ice with different concentrations of chlorine.   In Fig. 27. a, curve A shows the frequency characteristics of dielectric constant of pure ice (c//), in which dispersion occurs only in a frequency range from 10^2Hz to 5×10^4Hz and the dielectric constant has a constant value of 110 at lower frequencies.   When an extremely small quantity of chlorine (less than 10^{-6}M) was added, a slight deviation appeared at the frequencies below 10 Hz as shown by curve B, while the values above 10 Hz coincided with those of pure ice.   The deviation at lower frequencies increased as the chlorine concentration was raised.   This effect was attributed to space charge polarization near the electrodes, because it was observed to increase with the thickness of the specimen ; therefore, it is an extraneous effect instead of the intrinsic property of the doped ice itself.   On the other hand, the modification appearing around 10^3Hz is quite different from that observed at low frequency.   As discussed in detail in the two foregoing chapters, the addition of even a slight amount of KCl increased the values of dielectric constant of polycrystalline ice.   However, the incorporation of chlorine decreased the values of dielectric
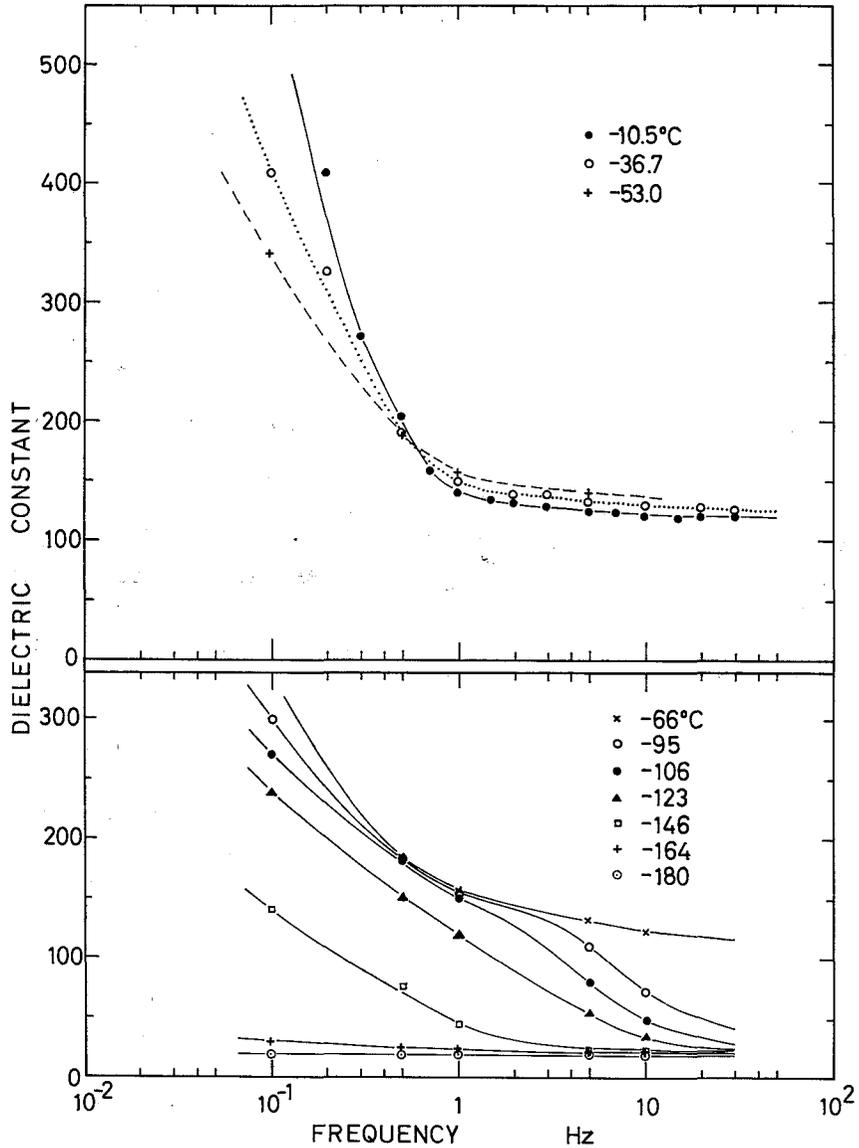
Fig. 28. Frequency dependence of low-frequency dielectric
constant for a single crystal of ice given by curve B in
Fig. 27. The parameter is the temperature, and the upper
diagram refers to temperature above −60°C and the lower
below −60°C

constant of single crystals as shown by curves C, D and E.   A similar effect was also noted in specimen D in Fig. 19.   The significant decrease of dielectric constant suggests that the orientational polarization of H_2O molecules in ice has been modified considerably by the chlorine incorporation.

The conductivity increased greatly with the addition of chlorine, espe-
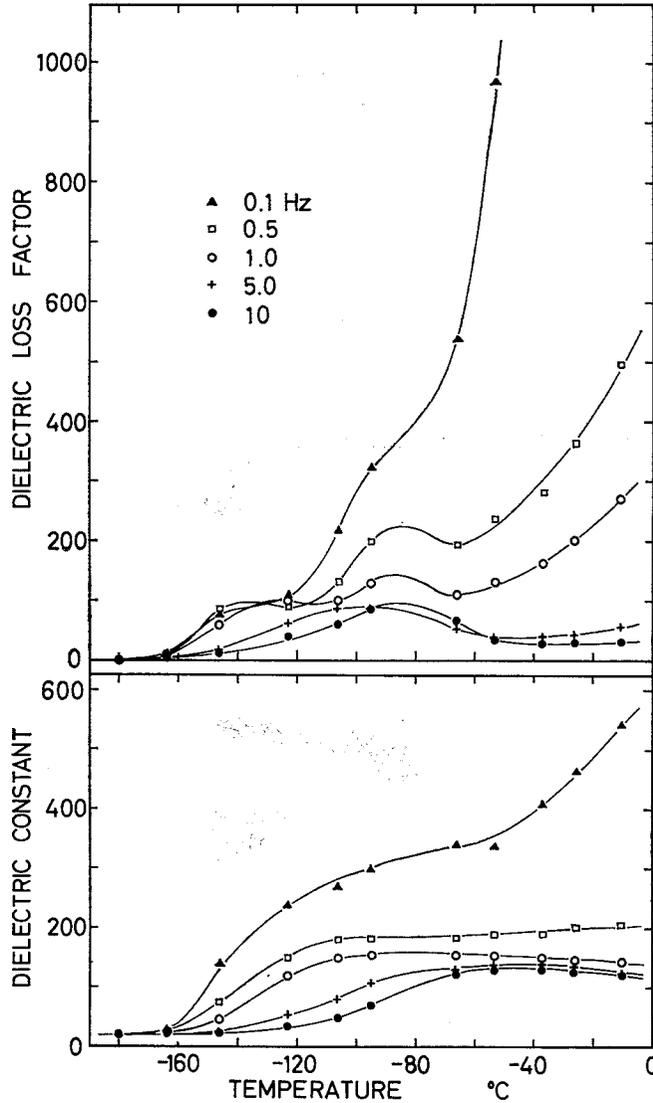

Fig. 29.   Temperature dependences of dielectric constant (lower) and loss factor (upper) of the same specimen as Fig. 28

cially at lower frequencies as shown in Fig. 27. b. This increase may be explained by the formation of some mobile charge carriers, which will be discussed later in more detail. These charge carriers cause space charge polarization near the electrodes and mask the true dielectric properties of the chlorine-doped ice when the chlorine concentration becomes higher, e. g., 1.4×10^{-5}M (F in Fig. 27). The dependences of dielectric properties both on frequency (in a low-frequency range) and temperature are shown in Figs. 28 and 29 for a single crystal of ice containing a very slight amount of chlorine (less than 10^{-6}M). As seen in these figures, the value of low-frequency dielectric constant decreased with the lowering temperature and gave a constant value of approximately 20 at $-180°$C. The temperature variations of dielectric constant of KCl ice were also observed by IDA et al. (1966), which were similar in a general aspect to those in Fig. 29, although their specimens were not single crystals. A drastic decrease of the dielectric constant at the low temperatures suggests the possible existence of ferro-electric transition in the chlorine-doped ice, but its details were not investigated this time.

IV. 3. *Mechanism of dielectric polarization and activation energies*

The chlorine incorporation into the single crystal of ice resulted in the significant decrease of the proper static dielectric constant. The mechanism of the modification does not seem simple. To find a clue to solve this subject, the relaxation time was estimated from the reciprocal of frequency at which the maximum loss occurred as shown in Fig. 30, and plotted against the reciprocal of the absolute temperature in Fig. 31. The activation energy was 5.76 kcal/mol, which is approximately the half of that obtained for pure ice, 13.5 kcal/mol.

The decrease in the values of static dielectric constant and activation energy compared with those of pure ice may be explained if we assume that chlorine ions are incorporated substitutionally in the forms of HCl molecules in the ice lattice. Since each of the HCl molecules introduces an L defect, which behaves in exactly the same manner as the thermally generated L defects, the depression takes place in the number of D defects and consequently in the value of dielectric constant, because the dielectric polarization in ice is governed by the majority defects which are D defects in pure ice (GRÄNICHER et al. 1957, JACCARD 1959). A similar explanation was made as to the small dielectric constants observed in HF-doped ice (STEINEMANN 1957), which also showed a small value of activation energy of 5.3 kcal/mol close to our value. YOUNG and SALOMON (1968) obtained
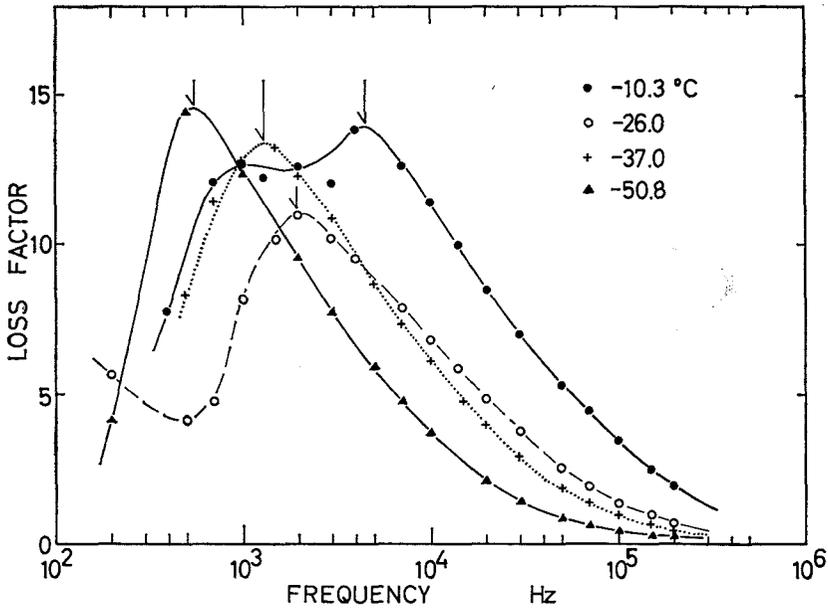
Fig. 30.   Frequency dependence of loss factor of a single crystal of ice containing 2.29×10^{-6} M chlorine.   Arrows indicate the positions of maximum
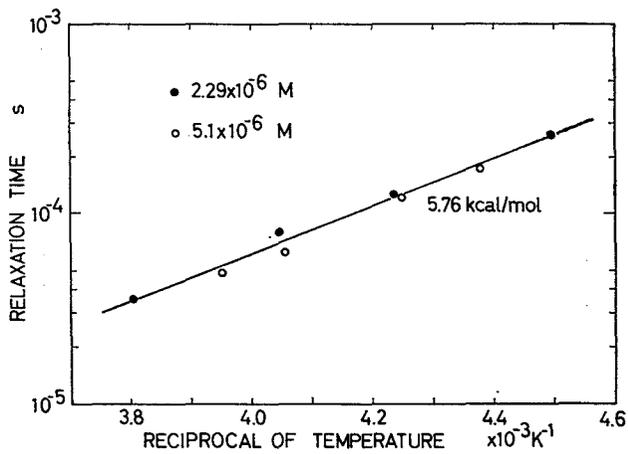

Fig. 31.   Dielectric relaxation time versus the reciprocal of the absolute temperature

a much larger value of 16.7 kcal/mol for HCl-doped ice, but they estimated the relaxation times by fitting the curves assuming that the dielectric dispersion of the HCl-doped ice could be precisely represented by Debye's equations with a single relaxation time. It should be noted, however, that the dielectric dispersions found in the impurity-doped ices can never be described by a simple single mechanism, as understood by the complicated frequency dependence of loss factor in Fig 30.

Figure 32 shows a relation between the low-frequency conductivity and the chlorine concentration. The low-frequency conductivity was estimated by extrapolation from the conductivities measured down to 0.1 Hz. As seen in this figure, the low-frequency conductivity is proportional to the square root of the chlorine concentration, which suggests that the substitutionally incorporated HCl molecules dissociate to create H_3O^+ ionic states and increase the low-frequency conductivity because the d. c. and low-frequency conductivities of ice are considered to be determined by the minority ionic
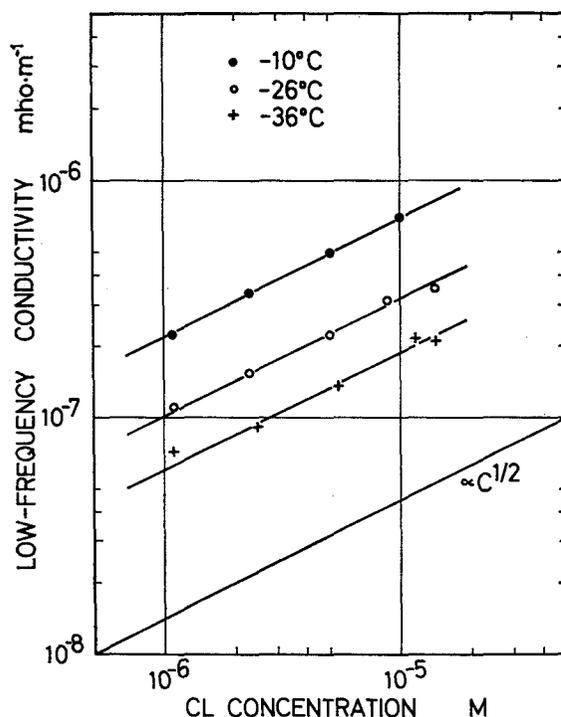

Fig. 32. Relation between the low-frequency conductivity and the chlorine concentration. The straight line drawn at the bottom shows the square root dependence upon the chlorine concentration

states (JACCARD 1959). The activation energy for the liberation of an H_3O^+ ionic state was estimated as 12.2 kcal/mol from the activation energy of the low-frequency conductivity (6.1 kcal/mol, Fig. 33) by assuming that the energy of proton jumps along a hydrogen bond was negligibly small (JACCARD 1959). GROSS (1965) measured the d.c. conductivity of ice grown from HCl solution and obtained an activation energy of 6.7 kcal/mol, which is in a good agreement with our value. YOUNG and SALOMON (1968) also found the square root dependence of the low-frequency conductivity in the case of HCl-doped ice, but reported that the activation energy increased with the HCl concentration from 2.25 kcal/mol (HCl concentration, 1.8×10^{-6}M) to 5.83 kcal/mol (HCl concentration, 1.0×10^{-5}M). In our measurements such a dependence was not observed. The difference of the results could be explained in part by taking account of their experimental procedure in which they estimated the low-frequency conductivity from the results only
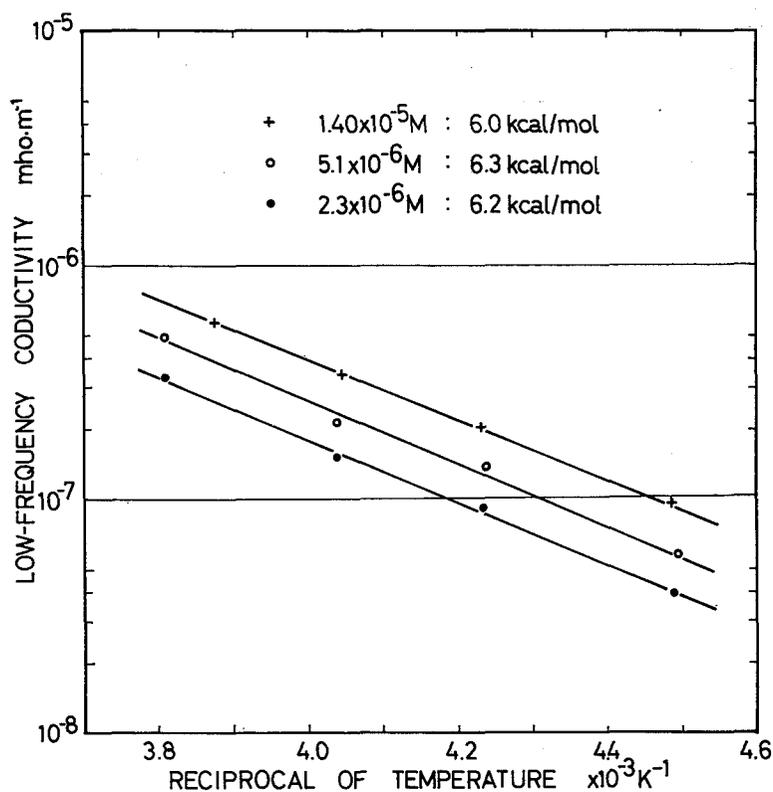

Fig. 33.   Plot of the low-frequency conductivity against the
reciprocal of the absolute temperature

obtained at the frequencies above 50 Hz, though they generally dispersed even below 50 Hz as seen, for example, in Fig. 27. b. However, the more possible and probably significant reason for the discrepancy would be the difference of the mode of the chlorine incorporation in the specimens through the variations of growing and ageing processes. There is no direct evidence to ensure the structurally homogeneous distribution of chlorine within single crystal of ice, though the dielectric properties observed for the chlorine-doped ice could be understood reasonably by the assumption of the substitutional incorporation and the subsequent dissociation of HCl molecules. Therefore, it may not be denied that the heterogeneous segregation of chlorine at sub-boundaries, which were first detected by TRUBY (1955) to form the hexagonal microstructures in ice, should play some roles in the dielectric properties and possibly other structure-sensitive properties, but the detailed structure of the sub-boundary has not been understood well.

IV. 4. *Conclusions*

It was found that, when a single crystal of ice was grown from KCl solution, a limited amount of chlorine was incorporated into the crystal lattice, but none of potassium was detected in the crystal. The maximum value of the chlorine incorporation was approximately $1 \times 10^{-4} M$.

The dielectric constant of chlorine-doped single crystals of ice decreased due to the incorporation and the activation energy for the dielectric relaxation reduced to 5.76 kcal/mol. The low-frequency conductivity increased as the square root of the chlorine concentration, and its activation energy was estimated as 6.1 kcal/mol. These experimental results could be explained by assuming that chlorine ions were substitutionally incorporated and dissociated, but a possibility of the heterogeneous segregation of chlorine at sub-boundaries was considered to be also likely.

V. Concluding remarks

In order to get a detailed knowledge about the dielectric behaviours of natural ices including sea and glacier ices, the dielectric properties of poly-crystals and monocrystals of ice grown from KCl solutions of various concentrations were systematically investigated in an extremely wide range of frequency, temperature and concentration. The results are summarized as follows: when the KCl concentration was higher than about $5 \times 10^{-3} M$, the dielectric properties of KCl ice above the eutectic temperature were greatly modified by the presence of the liquid solutions entrapped in the forms of brine pockets between thin ice platelets, showing extremely large values of

dielectric constant and conductivity compared with those of pure ice. Contributions from the liquid phase decreased considerably when the KCl concentration was less than 5×10^{-3}M.

When the temperature is lower than the eutectic point, all KCl contained in the ice changes to the solid phase, so that the dielectric values are considered to decrease as well. However, the effect of the KCl impurity on the dielectric properties could not be disregarded. In the high-concentration KCl ice ($>10^{-2}$M), two different dispersions were observed: the dispersion appearing in a higher frequency range could be represented by Debye's equations and its activation energy of relaxation was 5.3 kcal/mol; another dispersion was observed at much lower frequencies and its relaxation times were widely distributed. The dielectric dispersion found in the low-concentration KCl ice ($<10^{-2}$M) extended over an enormously wide range of frequency and was attributed to the polarizations occurring mostly near complex grain boundaries.

Chlorine ions were only found to be incorporated substitutionally into the crystal lattice of ice when it was grown from the KCl solution. The chlorine incorporation gave rise to a decrease in the static dielectric constant and the activation energy of the relaxation and an increase in the low-frequency conductivity. These results could be interpreted by the possible molecular processes of the substitutional incorporation and dissociation of HCl molecules in the ice lattice, but the contributions of sub-boundaries were also possible.

Acknowledgements

References

ADDISON, J. R. 1969 Electrical properties of saline ice. *J. Appl. Phys.*, **40**, 3105–3114.

ADDISON, J. R. and POUNDER, E. R. 1967 Electrical properties of sea ice. *In* Physics of Snow and Ice, part 1 (H. Ôura, *ed.*), Inst. Low Temp. Sci., Sapporo, 649–660.

ASSUR, A. 1958 Composition of sea ice and its strength. *In* Arctic Sea Ice, Nat. Acad. Sci.-Nat. Res. Council, USA, **598**, 106–138.

AUTY, R. P. and COLE, R. H. 1952 Dielectric properties of ice and solid D_2O. *J. Chem. Phys.*, **20**, 1309–1314.

BRADLEY, R. S. 1957 The electrical conductivity of ice. *Trans. Faraday Soc.*, **53**, 687–691.

BRILL, R., ENDER, H. und FEUERSANGER, A. 1957 Dielektrische Verhalten von Eis-Ammoniumfluorid-Mischkristallen. *Z. Elektrochem.*, **61**, 1071–1075.

BULLEMER, B. and RIEHL, N. 1966 Bulk and surface conductivity of ice. *Solid State Comm.*, **4**, 447–448.

DAVIDSON, D. W. and COLE, R. H. 1950 Dielectric relaxation in glycerine. *J. Chem Phys.*, **18**, 1417.

DEBYE, P. 1929 Polar Molecules. Dover Pub., Inc., New York, Chap. **V**.

EVANS, S. 1963 Radio techniques for the measurement of ice thickness. *Polar Record*, **11**, 406–410; 1966 Radio glaciology. *Cambridge Research*, November 1966.

FUJINO, K. 1967 a Electrical properties of sea ice. *In* Physics of Snow and Ice, part 1 (H. Ôura, *ed.*), Inst. Low Temp. Sci., Sapporo, 633–648; 1967 b Dielectric properties of sea ice. *Low Temp. Sci.*, **A 25**, 127–169.

GRÄNICHER, H., JACCARD, C., SCHERRER, P. and STEINEMANN, A. 1957 Dielectric relaxation and the electrical conductivity of ice crystals. *Disc. Faraday Soc.*, **23**, 50–62.

GROSS, G. W. 1965 Ion incorporation and activation energies of conduction in ice. *Ann. N. Y. Acad. Sci.*, **125**, 380–389.

HUMBEL, F., JONA, F. und SCHERRER, P. 1953 Anisotropie der Dielektrizitatskonstante des Eises. *Helv. Phys. Acta*, **26**, 2–32.

IDA, M., NAKATANI, N. and IMAI, K. 1966 Dielectric dispersion of impure ice at low temperatures. *Sci. Rep. Kanazawa Univ.*, **11**, 13–22.

JACCARD, C. 1959 Étude théorique et expérimentale des propriété électriques de la glace. *Helv. Phys. Acta*, **32**, 89–128.

KUROIWA, D. 1965 Internal friction of H_2O, D_2O and natural glacier ice. *CRREL Res. Rep.*, US Army, **131**, 1–45.

LANDOLT-BÖRNSTEIN 1960 Springer-Verlag Ohg., Berlin, **II**. 7 Teil, 87–89.

MAENO, N. 1972 Measurements of surface and volume conductivities of single ice crystals. Proc. Int. Symp. on Phys. and Chem. Ice held at Ottawa, August 1972, 24. 1–4.

MAXWELL, J. C. 1892 Electricity and Magnetism. Clarendon Press, Oxford, Vol. **1**.

MEAD, D. J. and FUOSS, M. 1941 Electrical properties of solids. XI. Polyvinyl acetate and polyvinyl chloroacetate. *J. Am. Chem. Soc.*, **63**, 2832–2840.

NAKAMURA, T. and JONES, S. J. 1970 Softening effect of dissolved hydrogen chloride in ice crystals. *Scripta Met.*, **4**, 123–126.

ONSAGER, L. and DUPUIS, M. 1962 The electrical properties of ice. *In* Electrolytes, Pergamon Press, Oxford, 27–46.

OSTERKAMP, T. E. and WEBER, A. H. 1970 Electrical phenomena accompanying the phase change of dilute KCl solutions into single crystals of ice. *J. Glaciol.*, **9**, 269–277.

RÖTHLISBERGER, H. 1967 Electrical resistivity measurements and soundings of glac-

iers : introductory remarks.   *J. Glaciol.*, **6**, 599–606.

SEIDENSTICKER, R. G. 1972 Partitioning of HCl in the water-ice system.   *J. Chem. Phys.*, **56**, 2853–2857.

SILLARS, R. W. 1937 The properties of a dielectric containing semi-conducting particles of various shapes.   *J. Instn. Elect. Engrs.*, **80**, 387–394.

SMYTH, C. P. and HICHCOCK, C. S. 1932 Dipole rotation in crystalline solids.   *J. Am. Chem. Soc.*, **54**, 4631–4647.

STEINEMANN, A. 1957 Dielektrische Eigenschaften von Eiskristallen II.   *Helv. Phys. Acta*, **30**, 581–610.

THE PHYS. SOC. JAPAN 1963 The Physics of Polymers. Asakura Shoten, p. 252 (in Japanese).

TRUBY, F. K. 1955 Hexagonal microstructure of ice crystals grown from the melt.   *J. Appl. Phys.*, **26**, 1416–1420.

WAGNER, K. W. 1924 Die Isolierstoffe der Elektrotechnik. Springer, Berlin.

WASHBURN, E. W. 1928 Int. Crit. Tables. McGraw Book Co., Vol. **IV**. 259.

WEAST, R. C. 1968 Handbook of Chemistry and Physics. Chemical Rubber Co., D-93.

YOSHINO, T. 1961 Radio wave propagation on the ice cap.   *Antarctic Record*, **11**, 228–233.

YOUNG, I. G. and SALOMON, R. E. 1968 Dielectric behavior of ice with HCl impurity.   *J. Chem. Phys.*, **48**, 1635–1644.

ZAROMB, S. and BRILL, R. 1956 Solid solutions of ice and NH_4F and their dielectric properties.   *J. Chem. Phys.*, **25**, 350–356.