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Measurement of electrical conductance in ice cores by AC-ECM method

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Abstract: A relation between ice electrical conductance and impurity ions incorporated in ice was investigated from several samples of Antarctic and Arctic ice cores. Conductance was measured using the AC-ECM method. The aim of this study was to assess the possibilities and limitations for rapid detection of impurity ions in polar ice cores through measurements of electrical conduction. We are in particular interested in higher spatial resolution with which we can investigate if there is a contrast of electrical conductivity, between ice-grain boundaries and within the ice-lattice. We found that there is a proportional relation between the high-frequency conductance and molarity of sulfuric acid in the ice cores. In addition, the observed relation (molar conductance) was consistent with the molar conductivity found in earlier studies at LF and microwave frequencies. Moreover, we found that sodium chloride can also increase the conductance. The results suggest that AC-ECM is a useful method for rapid, quantitative, and high-resolution detection of these constituents in ice cores. A preliminary high-resolution analysis using doped ice showed that electrical conductance is localized in the vicinity of grain boundaries in case of doped ice. Based on these tests, the method was recently used for ice analysis of the 2504-m-deep Dome Fuji station ice core.

1. Introduction

In ice core studies, measurements of electrical properties of solid ice are often used for rapid detection of impurity ions incorporated in the ice lattice and at grain boundaries. A high voltage direct-current

method, known as ECM invented by Hammer [1], has been used for detection of acidic layers in many Arctic and Antarctic ice cores. On the other hand, the AC method, developed by Moore and Paren [2], is known as DEP (dielectric profiling). In addition to acidity detected by ECM, the research group

who developed DEP [3, 4] have found that mainly acids, ammonium, and chloride contribute to increases of high-frequency conductivity. The physical mechanism of electrical conduction is explained by Jaccard-theory-based conduction; protonic conduction occurs at and along point defects in an ice lattice and/or by localized impurities at grain boundaries [5].

A limitation of the present understanding is, however, that we do not know yet clearly the relative role of each conduction mechanism, at defects in the crystal-lattice (point defects), at two-grain boundaries (plane defects), and at three-grain boundaries (intergranular paths). One consequence of this is the recent argument about DC conduction mechanism observed by electrical resistivity sounding in Antarctica [6-8]. Wolff et al. [5] reviewed the conduction mechanism at DC and in the high-frequency-limit range, based on the statistical analyses from a huge number of data from the ice core analyses (both electrical measurements and chemistry). They discussed that the dominant component of high-frequency conductivity can be explained by Jaccard Theory (conduction occurs at point defects in the ice lattice). They also discussed that it is possible that DC conduction (and therefore probably some part of AC conduction) is explained by conduction in the liquid phase at intergranular paths. Indeed, in ice containing acid impurities, some experimental works [9, 10] suggest that some component of electrical conduction may be explained by conduction in the liquid phase in ice. For better and systematic understanding, we need more information on how impurity ions are distributed and localized in polycrystalline ice. The better understanding is important also to interpret roles of impurity ions for

mechanical properties in ice sheets [11]. However, no methods have been available to detect localized conductivity in the scale range of crystal grains (less than several mm).

In addition to the two established ice-core analysis techniques (ECM and DEP), improvements of the electrodes and methods have been attempted [12-15]. These attempts have aimed at higher spatial resolution and/or higher precision of the measurements. One of these attempts was an AC method tested by Sugiyama et al. [14] with 2-terminal electrodes. This method was named AC-ECM because electrodes' geometry is the same as that of the original (DC-)ECM. Some features of AC-ECM are, 1) higher spatial resolution measurement by slow scanning of ice without any space-charge build-up, and 2) high-frequency information at 1 MHz and at 1 V. These features allow us to scan the ice surface to investigate microscopic properties by taking smaller electrode separation. Sugiyama et al. [14] investigated an optimum frequency and ice temperature suitable for AC-ECM. They showed that surface conductance measured by AC-ECM is proportional to conductivity and that frequency of 1 MHz and temperature below -20°C are optimum conditions. In this paper, we report results of further tests of this method using ice cores from Arctic and Antarctic ice, in order to investigate the validity of the method for ice core analysis. Based on the investigations described here, we used this method for analysis of the 2504-m-deep Dome Fuji station ice core. AC-ECM analysis of the Dome Fuji core was carried out from 1995 to 1998. Data are currently being analyzed.

2. Method and procedure

2.1. System and electrodes

The details of the system are described in Sugiyama et al. [14]. The system consists of 2-terminal coaxial electrodes and a precision LCR meter (HP4284A). We can measure complex admittance ($Y^* = G + Bi$; G: conductance and B: susceptance) at a point of the ice core surface at arbitrary frequencies between 20 Hz and 1 MHz. In our measurement we used mainly 1 MHz because it is suitable to detect the high-frequency limit conductance of ice [14]. Only for a part of ice samples, we investigated the frequency dispersion. The experimental set up is illustrated in Figures 1 (a) and (b). The distance between electrodes is 10 mm in this study in the direction perpendicular to the core axis. The effective spatial resolution along the core axis was a

few millimeter in this case, which is the width where there are majority of the lines of electric force.

2.2. Ice samples

We used polar ice samples from two sites in the Antarctic ice sheet and from one site in the Arctic ice cap. Among these three samples, two contain acidity peaks due to sulfuric acid. The other contains high concentration sodium chloride. Through investigation of these three samples, we examined the effect of sulfuric acid and sea salt. In addition, we used sulfuric-acid doped ice to see if electrical conductivity is localized or not.

2.2.1. Ice core from the South Yamato meteorite ice field.

One of the samples is from an ice core drilled at South Yamato (Hereafter we describe it as SY ice.) meteorite ice field,

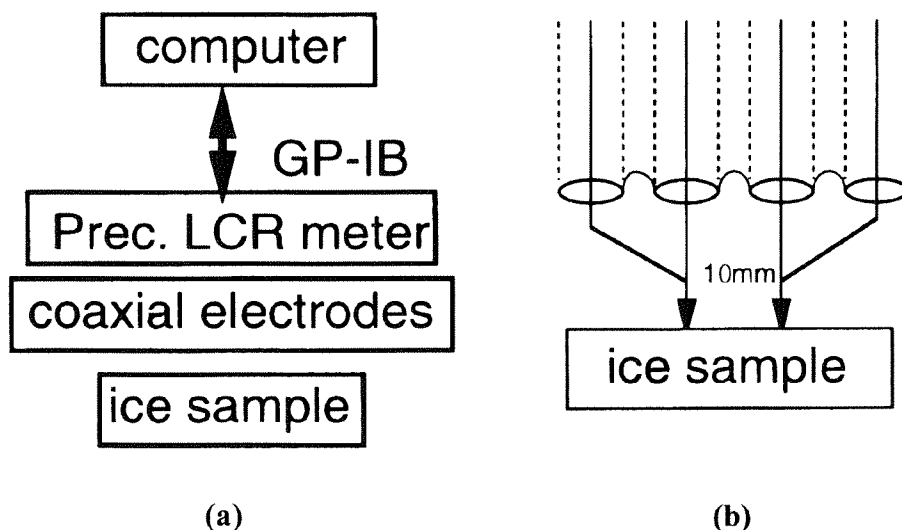


Figure 1: (a) Schematic diagram of the AC-ECM system. It consists of the electrodes and a precision LCR meter (HP4284A). (b) AC-ECM electrodes. They form a 4-terminal network. Two of them are in direct contact with the ice surface. The two outer terminals are connected to the inner terminals near the ice surface.

Table 1: List of ice core samples.

Core and ID number	Depth of core top (meter)	Core length (meter)
1. South Yamato meteorite-field ice core [16, 10]		
SY36	15.45	0.45
SY42	18.21	0.50
2. Agassiz Ice-cap core [17]		
Agassiz59	55.96	0.74
3. Nansen meteorite-field ice [10, 14, 18, 21]	0.50	0.20

Antarctica [16]. The original ice core was 101.4 m long but we measured the depth range from 17 m to 23 m for this study. Because we detected two large conductivity peaks due to acidity from past volcanism at depths of 15.6 m and 18.4 m, impurity ions were analyzed using ion-chromatography for these two portions. Chemical analysis was carried out by K. Osada and M. Kido at Nagoya University. This 15.6 m peak was also investigated recently by Fukazawa et al. [10] with Raman spectroscopy. They irradiated the triple junctions of grain boundaries with laser light, and detected a peak-spectrum signal. They interpreted that SO_4^{2-} ions exist in the liquid phase. Although our AC measurements were done at 1 cm intervals at this stage (later we measured the Dome Fuji station ice core continuously), the resolution of the chemical analyses was 3 cm. Therefore we needed to resample when we compared the AC conductance with the results of chemical analyses. As a result of chemical analysis, we understood that the major component of the two acidity peaks was sulfuric acid.

2.2.2. Ice core from the Agassiz Ice Cap.

Another ice sample was from the Agassiz Ice Cap, Arctic Canada. Hereafter we describe it as Agassiz ice. An ice core was drilled on the summit of the Agassiz Ice Cap, Ellesmere Island, Canada [17] in

April-May 1993. The core was drilled down to the bedrock at 123 m depth with an electro-mechanical drill. We used only several 50-cm long portions of the core for the AC-ECM analysis. Through the test analysis of the AC-ECM electrodes, a conductivity peak was detected at a depth of 56.2 m. This conductivity peak is the same as the 1259 AD peak detected by DC-ECM [18]. Therefore, analysis of impurity ions was carried out for this portion of the sample. Chemical analysis was carried out at Nagaoka Institute of Snow and Ice Studies. We found that major component of the acidity peak was sulfuric acid (Figure 2) also in this ice.

2.2.3. Ice from the Nansen meteorite ice field.

The possible effects of sodium chloride component and of temperature were investigated using a sample collected from the Nansen meteorite ice field in East Antarctica. Hereafter we describe this as Nansen Ice. Ice was originally collected in 1988 by the 29th Japanese Antarctic Research Expedition meteorite search team using a chain-saw from ice that contained visible volcanic tephra [19, 20]. This ice has been used for several ice studies [10, 14, 21] in the past. Chemical analysis was carried out at National Institute of Polar Research in 1991 [21]. This ice contains high-level

Table 2: Chemical component in Nansen ice [14, 24].

Ion	Na ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	K ⁺
Concentration (μM)	35.4	29.3	6.6	4.1	4.8

sodium chloride, a few kinds of low concentration ions, and volcanic tephra (see Table 2). The major impurity ion is sodium and chloride. For acidity we did not carry

out any pH measurement nor acid titration. Because we did not measure Ca ion nor Mg ion, acidity in this ice could not be determined from the ion balance.

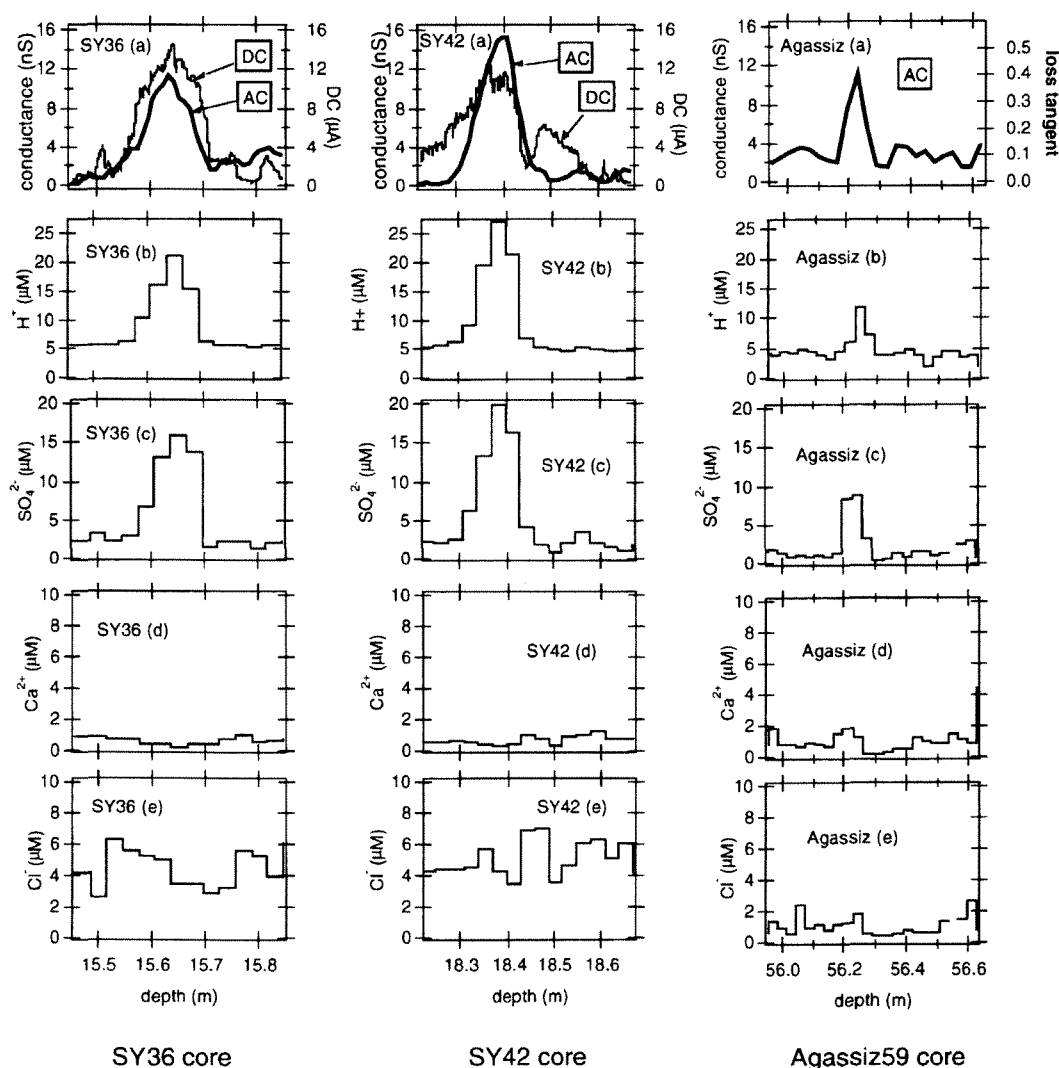


Figure 2: AC-ECM signal, DC-ECM signal and concentration of major ions for three ice core samples. SY36 sample (left), SY42 sample (middle), and Agassiz59 sample (right).

Nevertheless this sample was used to investigate the response of conductance to the constituents (mainly sodium chloride) in this sample. In addition, temperature effects were investigated in the temperature range between $-20\text{ }^{\circ}\text{C}$ and $-80\text{ }^{\circ}\text{C}$.

2.2.4. Doped ice.

Sulfuric-acid-doped polycrystalline ice was prepared with the same procedure as earlier studies [9, 22]. Aqueous solution was frozen in a plastic bag. The concentration of sulfuric acid was about 1 mM. We measured the conductance of the ice surface by setting both electrodes in the vicinity of the grain boundaries or in the ice lattice away from grain boundaries.

3. Results and discussion

3.1. SY ice and Agassiz ice

Results of electrical measurements and chemical analysis are shown in Figure 2. For SY ice and Agassiz ice, all the measurements were done at a temperature of $-20 (\pm 1)\text{ }^{\circ}\text{C}$. Electrical conductance ranged up to 16 nS according to impurity concentration. Only the chemical analysis results for sulfate, calcium, chloride and hydrogen are shown. Hydrogen concentrations are all from pH measurement and not from acid titration. We found that electrical conductance increases linearly with sulfuric acid concentration. For the other anions and cations, we found no clear correlation with electrical conductance. DC-ECM analysis was also carried out for SY samples for comparison. They are shown with the AC-ECM results. We found that there is only a rough correlation between acid concentration and DC signals. There is also an anti-correlation between chloride and DC-signals. But chloride had no clear effect on AC signals, as far as can be determined

from our data. It seems that there is a rough correlation between DC signal and acidity; the apparent effect of chloride suggests a need for reconsideration of earlier simple conclusions that DC conductance is a function of only acidity [3, 5]. Standard deviations and factors that cause the deviations should be examined. A similar result was obtained by K. Matsuoka [23], who investigated both AC- and DC-ECM conductance using an Arctic ice core from Svalbard.

The relation between sulfuric-acid concentration and AC-signals is plotted in Figure 3. We find that the conductance increases linearly with acid concentration. The conductance arising from the presence of acid (that is, molar conductance) is about $0.7 \times 10^{-3} (\text{SM}^{-1})$. Considering that the ratio between AC conductance from our AC-ECM electrodes and conductivity in ice is 5×10^3 (an empirical ratio for the electrode at this stage) we calculate that the molar conductivity is about $3.3 (\pm 0.8) (\text{Sm}^{-1}\text{M}^{-1})$. This is almost the same as the molar conductivity of ice containing sulfuric acid measured at LF and microwave frequencies at the same temperature, $-20\text{ }^{\circ}\text{C}$ (see Table 3). We tentatively interpret that this agreement suggests as follows: 1) the electrical conduction mechanism due to presence of sulfuric acid is common between polar ice cores and doped samples; 2) with conductance measured by AC-ECM, we can derive electrical conductivity by finding a proper coefficient for each AC-ECM electrode. The first interpretation cannot yet be conclusive because the agreement of the values can be only accidental. We should confirm later whether or not the distribution of the acidity and its effect on electrical conduction are the same. The AC-ECM method is the only method available for this

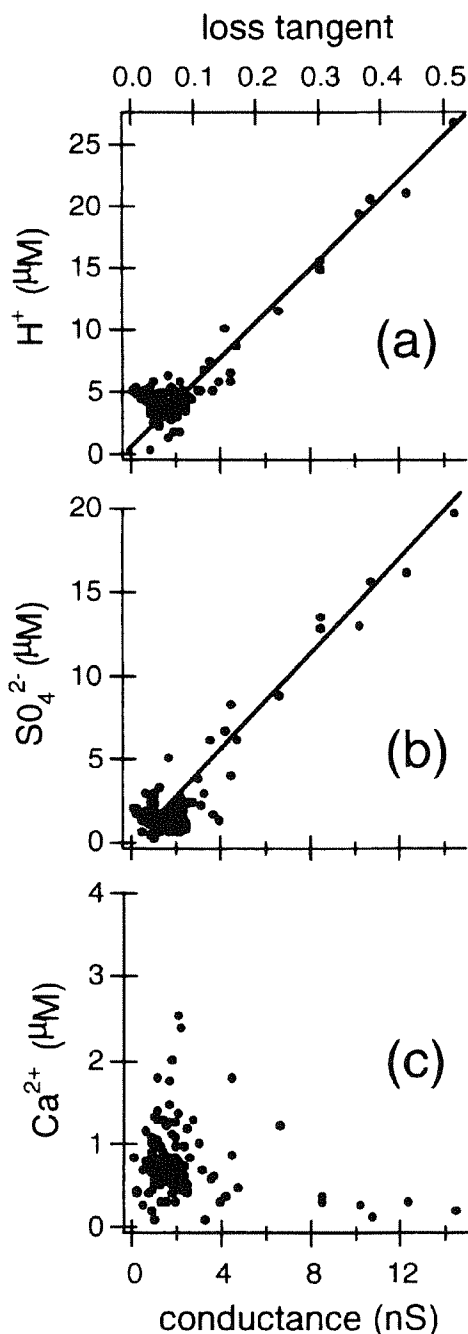


Figure 3: Conductance measured by AC-ECM and concentration of major ions for all samples. We find a linear relation between conductance and sulfuric acid concentration.

purpose. The latter interpretation means that we can detect localized conductivity with AC-ECM electrodes by making electrodes' separation smaller.

We should comment some experimental uncertainties in the results. For, we cannot explain yet adequately some feature of our data. One example is that conductivity is close to zero even when hydrogen ion is close to $5 \mu M$ (in Figure 2, SY42 (a-c)). Another example is that conductance of pure ice components does not seem to appear in the results (for example, in Figure 3). We need to investigate reason of these in further analyses of the AC-ECM data.

3.2. Nansen ice

Figure 4 shows variations of AC-signals with changing temperature, measured from Nansen ice. Nansen ice is characterized by high concentration of sodium chloride and low concentration of a few other ions (see Table 2). Note that Mg or Ca was not investigated. Therefore ion balance cannot be determined until we carry out acidity measurement. At the optimum experimental condition of AC-ECM (frequency at 1 MHz and temperature at $-20^\circ C$, conductance is about 25 nS. According to Sugiyama et al. [14], the conductivity of this ice is about $40 (\mu S/m)$. Although this conductivity level is not as high as the conductivity found in SY42 sample (about $80 \mu S/m (=16 nS \times 5000)$), it is still very high level for ice in the ice sheet. This increase tentatively suggests that those impurities including sodium chloride in Table 2 was the cause although we need to investigate the acidity in this sample.

Results of the measurements show typical Debye-type dielectric dispersion (Figures 4(a) and 4(b)). Conductance increases in a step at around the relaxation

Table 3: Molar conductivity of ice containing strong acids at $-20\text{ }^{\circ}\text{C}$ (Experimental Data).

Reference Number	Sample	Kind of Acid	Concentration	frequency	Molar Conductivity ($\text{Sm}^{-1}\text{M}^{-1}$)	Activation Energy (eV)
This study	ice core	H_2SO_4	1-20 μM	1 MHz	3.3 (± 0.8)	-
3-5	ice core	H^+	0-30 μM	-300 kHz	3.3 (± 0.8)*1	0.22
9	doped	H_2SO_4	197 μM	5 GHz	3.5 (± 0.2)	0.16
	doped	HNO_3	119 μM	5 GHz	2.4 (± 0.2)	0.15
21	doped	H_2SO_4	0-14 mM	1 MHz	2.7	-
26	ice core	H_2SO_4	0-10 μM	250 kHz	3.9 *2	-
20	doped	$\text{H}_2\text{SO}_4, \text{HNO}_3, \text{HCl}$	2-35 mM	9.7 GHz	3.7 (± 0.2)	0.19

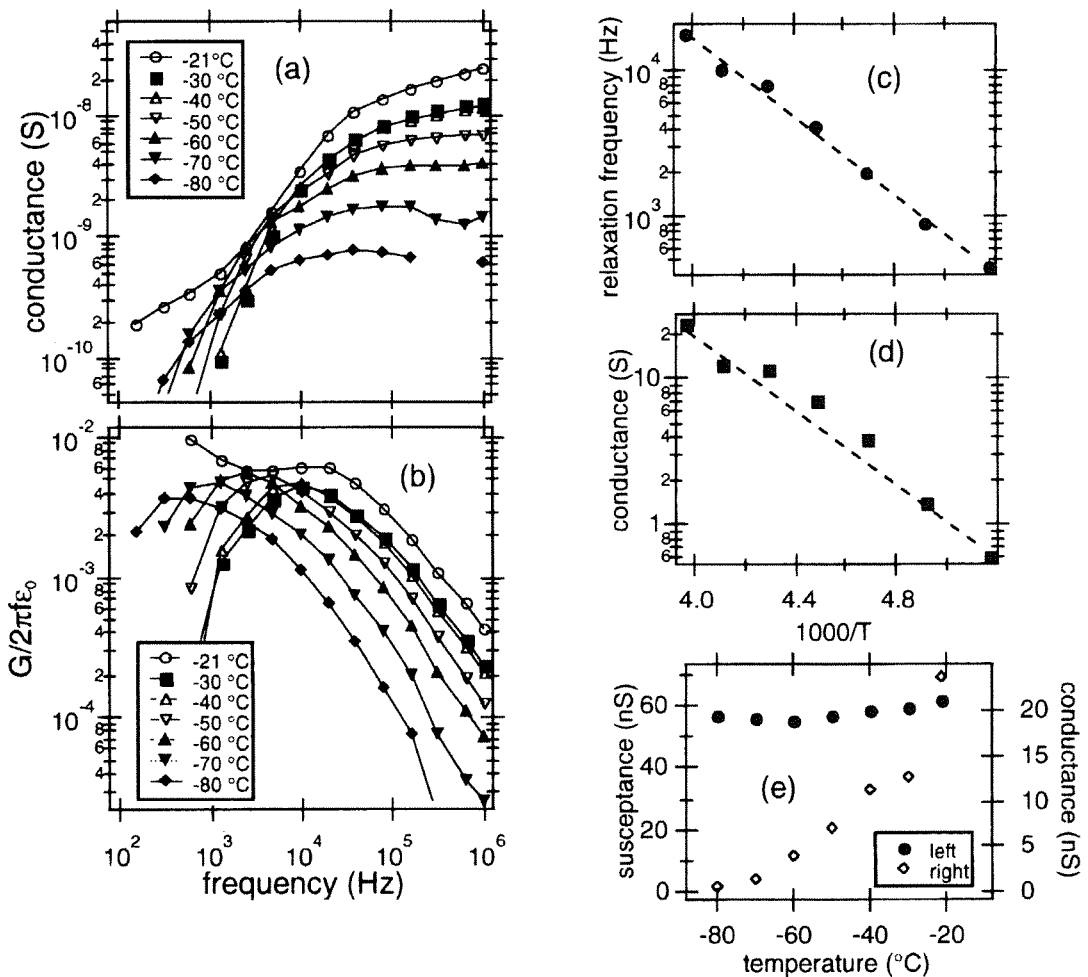
*1 corrected value from a value 4 (± 1) at $-15\text{ }^{\circ}\text{C}$.*2 corrected value from a value 3.66 at $-22\text{ }^{\circ}\text{C}$.

Figure 4: Temperature dependence of AC-ECM signals from Nansen ice sample. (a) Debye-type dispersion of conductance. (b) A quantity, $G/2\pi f\epsilon_0$, proportional to the imaginary part of the dielectric permittivity. (c) Relaxation frequency of Debye-type dispersion (Arrhenius plot). (d) Temperature dependence of conductance (Arrhenius plot). (e) Complex admittance (susceptance, B, and conductance, G) at 1 MHz.

frequency in kHz range (see Figure 4(c)); the high-frequency limit conductance was attained at 1 MHz. A general interpretation of this dispersion is given in the standard reference on physics by Petrenko [24]. What we learn from this observation is that electrical conductance is due to orientational polarization of water molecules at lattice defects (point defects and/or perhaps plane defects (grain boundaries)). Normally, the high-frequency limiting conductivity of ice is more than 10^3 times larger than the DC conductivity [24]. Our example of frequency dispersion also suggests that AC-ECM signals are more than 10^3 times larger, which enables us to detect the conductance without using high voltage as does DC-ECM, which normally uses a voltage between 100 and 2000 V. The activation energy of the electrical conduction was 0.25 (± 7 % (standard deviation)) eV, calculated from the conductance in Figure 4(d). This value is similar from other studies of ice.

Another interesting feature of the result is that the susceptance at 1 MHz increases slightly with temperature (see Figure 4(e)). The susceptance is basically closely connected to the real part of complex permittivity. The behavior of the profile (slight increase with increasing temperature) is very similar to that of the real part of the dielectric permittivity of ice. An interesting possibility is that by calculating loss tangent (equal to G/B), we can obtain loss factor which is a dimensionless number. In this case the calculated values should be independent from geometry or size of the electrodes. Anticipating future analysis of the AC-ECM results as loss tangent, scales by loss tangent are prepared in Figures 2 and 3.

3.3. Doped ice

The sketch of the surface of ice and locations of the electrodes on it is shown in Figure 5. Size of each crystal grain in ice was between a few mm and about 20 mm. 10 different locations of the electrodes are also indicated in the figure. The conductance measured at each position of the electrodes are listed in Table 4. From data in Table 4, electrical conductance in the vicinity of grain boundaries was 24 ± 3 nS (mean value and the standard deviation), 4 times higher than the conductance away from grain boundaries, 6 ± 3 nS. This result simply suggests that electrical conduction is localized in the vicinity of grain boundaries in case of doped ice. The grain boundary effectively constitutes the conduction path in this case.

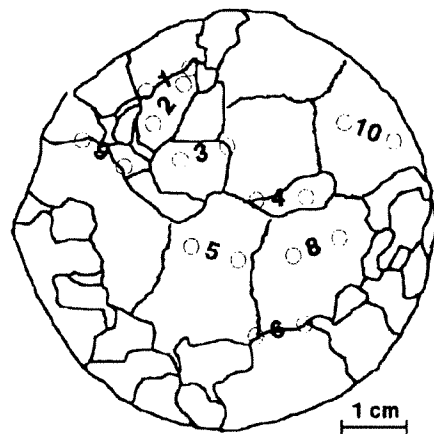


Figure 5: Distribution of the grain boundaries on the surface of acid doped ice used for investigation. Diameter of the crystal grain is about from 2 mm to 20 mm. Position of the two-terminal electrodes are shown with numbers. The results are listed in Table 4. Note that position of No. 7 was not recorded. But it was recorded that the electrodes were on the grain boundaries just like 1, 6, and 9.

Table 4: Conductance of acid-doped ice.

Position of Electrodes in Figure 5	conductance (nS)
In the vicinity of grain boundaries.	
1	24
3	17
4	19
6	18
7*	27
9	38
Away from the grain boundaries.	
2	12
5	8
8	3
10	3

* For this measurement, position was not recorded in Figure 5.

4. Conclusions and further studies

From our AC-ECM measurements of polar ice and doped ice, we conclude as follows.

1) The relation between the high-frequency conductance and molarity of sulfuric acid is linear. Moreover, the observed value of molar conductance was in good agreement with values obtained in earlier studies at LF and microwave frequencies. However, we cannot yet determine whether or not the agreement between polar ice and doped ice is accidental, until we confirm that the conduction mechanism and localization of conductance are common between them.

2) Measurement of Nansen ice tentatively suggested that sodium chloride also increased the conductance. This feature is common with the dielectric profiling method (DEP).

3) The results suggest that AC-ECM is a useful method for rapid, quantitative, and high-resolution detection of sulfuric acid and probably sodium chloride in ice cores. This

feature is a combination of two well-known methods, ECM and DEP.

4) By applying this method to ice doped with sulfuric acid, we found that electrical conduction is localized in the vicinity of the grain boundaries, at least in case of this ice.

Based on the results of these tests, the AC-ECM method was recently used for ice analysis of the 2504-m-long Dome Fuji station ice core. The huge number of measurements are currently being analyzed. At the moment, the role of acid ions localized in grain boundaries and its effect to dc conductivity is still an open question. At least, some observations suggest that sulfuric acid is localized at grain boundaries in the liquid phase [9, 10, 25]. As for conductivity component which appears only in AC (AC high frequency limit conductivity) point defects in the ice lattice should be responsible according the Jaccard theory. In particular for non-acid part of ac conduction, Bejrrum L and D defects are important [5]. We did not investigate localized conductivity of polar ice cores.

Further investigation using 2504-m Dome Fuji ice cores is currently in progress. We expect that it will provide data set that can systematically solve this problem in the near future. Further understanding of this problem will help us to know how impurity ions are preserved in polar ice and how they control the electrical and mechanical properties of ice.

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