

Dielectric Dispersion of Impure Ice at Low Temperatures*

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1. Introduction

While the dielectric behavior of ice has been investigated by many authors, but very few of them seem to have carried out the measurement at temperatures as low as that of liquid air. This may be due to pure ice showing no conspicuous dielectric dispersion at very low temperatures. Shishikura and Kakiuchi⁽¹⁾ found an anomalous dielectric dispersion of ice at temperatures near 100°K, when it had been doped with 0.001N KOH.

On the other hand Dengel et al⁽²⁾ reported that the ferroelectricity of ice appeared at very low temperatures about 100°K, with a relaxation time of the order of hours, if the water used for the crystal growth was not extremely pure.

In the present experiment the dielectric measurement of impure ice was made mainly at frequencies as low as a few c/s and at temperatures over the range above -190°C, and KOH, NaOH, LiOH, NH₄-OH, Ba(OH)₂, KCl, HCl, HF, NH₄F and H₂O₂ severally were employed as the impurity.

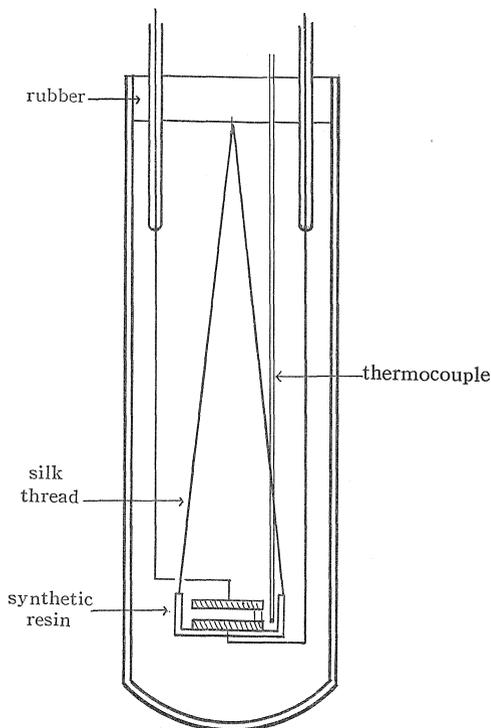


Fig. 1 The cell used for the dielectric measurement.

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2. Experimental Procedure

The features of the cell employed are shown in Fig. 1. Two gold plated brass electrodes (diameter : 20mm) were insulated by three polystyren spacers (thickness : 2.4 mm) making the capacitance in the air $1.1 \mu\mu\text{F}$. The temperature control was effected by raising or lowering the glass jar containing the cell and partly immersed in a liquid air bath. The temperatures were measured by a copper-constantan thermocouple and a microvoltmeter. The dielectric measurements were carried out with the apparatus described previously⁽³⁾. The water was made to become ice abruptly by cooling it with liquid air, and the measurement was made mainly in the heating stage.

3. Experimental Results and Discussion

Pure ice

For comparison, the dielectric dispersion of pure ice obtained from conductivity water of specific conductance of about 2×10^{-6} mho/cm was measured. The temperature dependence of the real part of the dielectric constant in the heating stage at 1000 c/s, 200 c/s, 25 c/s, 5 c/s and 1 c/s is shown in Fig. 2 and the Cole-Cole diagram at -61°C is shown in Fig. 3. In the calculation of the values of ϵ'' correction for the errors due to dc conductivity was not made because they were negligibly small compared to the total conductances. Similar approximation was adopted in all the later calculation of ϵ'' . From Fig. 2 we see that dielectric dispersion occurs only above about -100°C , which is closely related to the transition temperature of cubic and hexagonal structure of ice. The Cole-Cole diagram in Fig. 3 shows that the dispersion is of the Debye type with some distribution of relaxation times added with another type dispersion originating at lower frequencies. This second type dispersion was found by Humbel et al⁽⁴⁾ only above the temperature -20.5°C , although in their experiment,

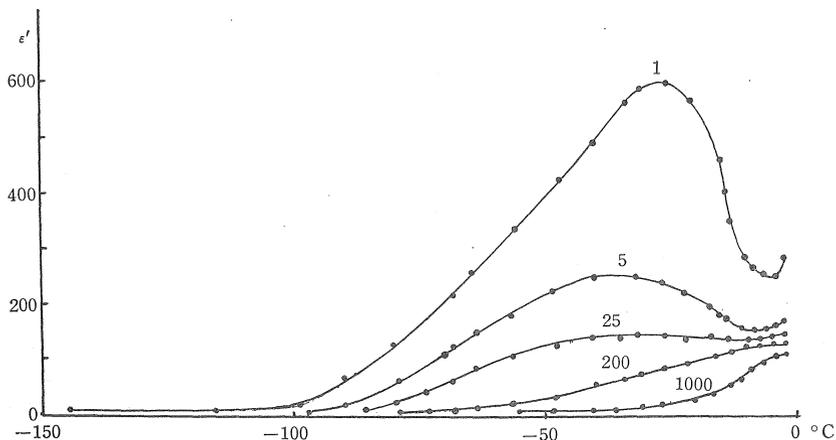


Fig. 2 The temperature dependence of ϵ' of pure ice.

frequencies higher than 50 c/s were used. Furthermore their Cole-Cole diagram is a semicircle showing that the relaxation time of the dispersion is not distributed. The

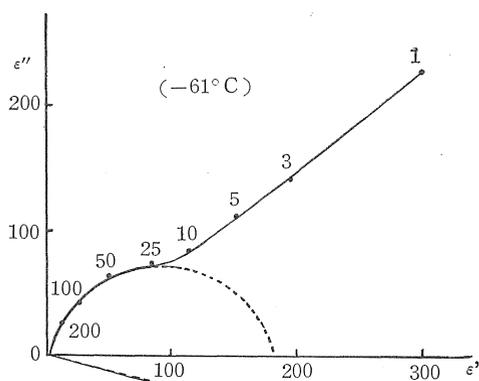


Fig. 3 The Cole-Cole diagram of pure ice at -61°C .

origin of these differences between the results of the authors and Humbel et al perhaps may be due to the higher impurity of the ice in the present experiment.

The mechanism of the Debye type dispersion must be explained by the orientational motion of water molecule of Bjerrum's theory.⁽⁵⁾ And the second type dispersion at low frequencies seems to be explained by the space charge polarization theory of Macdonald⁽⁶⁾ in the same manner as Steinemann and Gränicher⁽⁷⁾

discussed, because the dielectric constant of the dispersion ϵ' increases with the increase of the thickness of ice.

Caustic alkali-doped ice

Shishikura et al⁽¹⁾ studied the dielectric dispersion of ice doped with KOH to the concentration of 0.001 N. In the present experiment the concentration of KOH was varied over a wide range.

The temperature dependence of the real part of the dielectric constant of ice doped with 0.008N KOH is shown in Fig. 4, from which we see that a dielectric dispersion occurs even below -190°C and increases abruptly at a temperature near -100°C . In this paper two dispersions observed below and above the temperature about -100°C are called as dispersion A and B respectively. As the concentration of KOH increases, dispersion A becomes larger and reaches a limit at about 0.03N. The result for 0.1N concentration is shown in Fig. 5, and the Cole-Cole diagram at -142°C is shown in

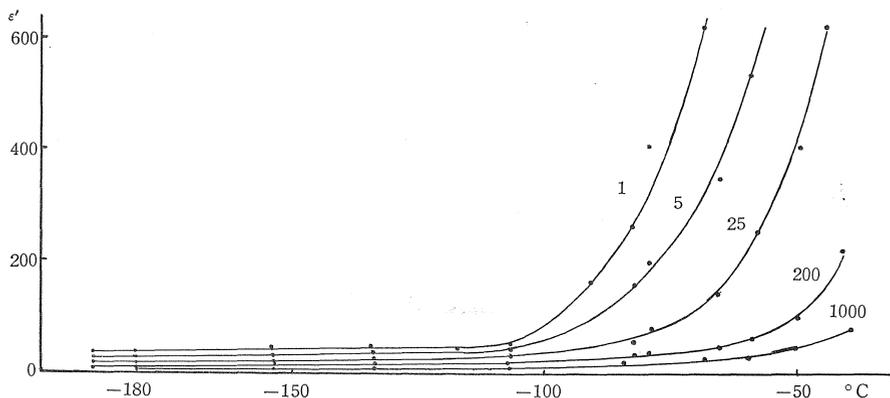


Fig. 4 The temperature dependence of ϵ' of ice doped with 0.008N KOH,

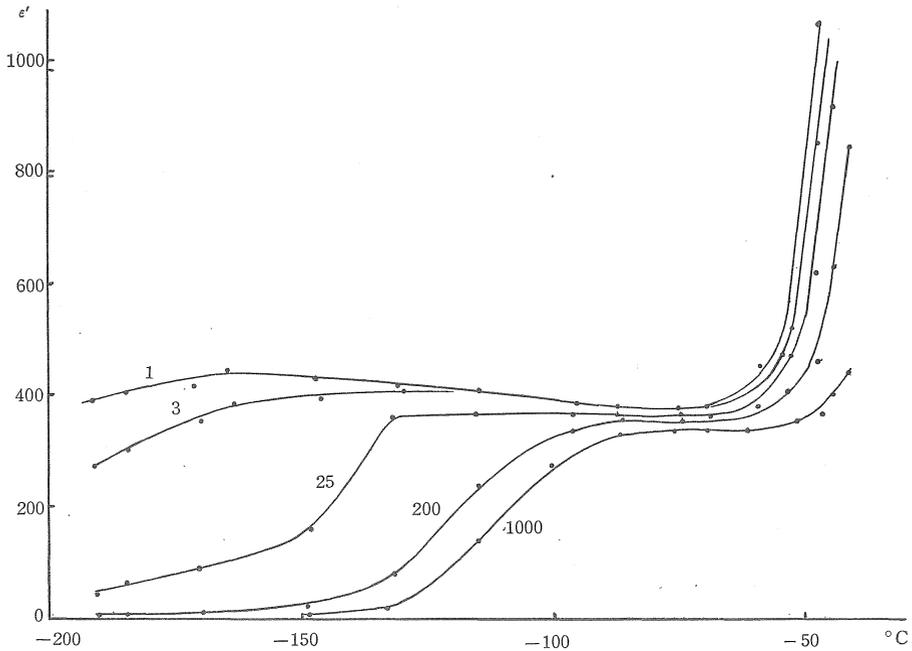


Fig. 5 The temperature dependence of ϵ' of ice doped with 0.1N KOH.

Fig. 6. From the diagram dispersion A seems to be of the Debye type with some distribution of relaxation times, but not to be accompanied by another type dispersion such as occurs in pure ice at -61°C and was attributed to the space charge polarization. The relaxation time for each temperature was estimated as the inverse of the frequency corresponding to the maximum value of ϵ'' . The temperature dependence of the relaxation time is shown in Fig. 7. The activation energies calculated from the curve are between 0.65 and 3.7 Kcal/mol. These values are approximately equal to or smaller than the figure 2.5 Kcal/mol reported by Bjerrum⁽⁵⁾ for orientational

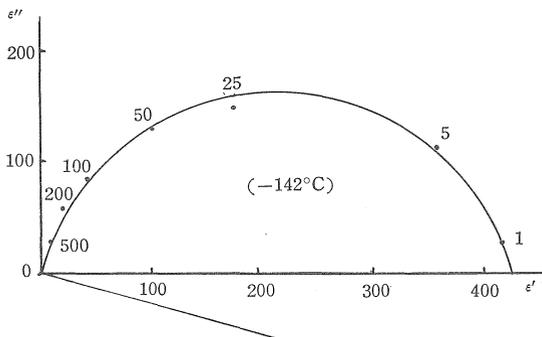


Fig. 6 The Cole-Cole diagram of ice doped with 0.1N KOH at -142°C .

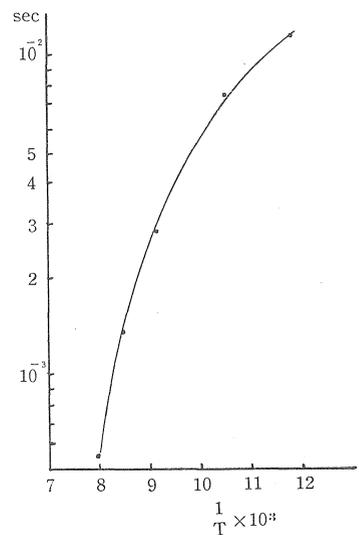


Fig. 7 The temperature dependence of the relaxation time.

polarization of ice caused by lattice defect. In this case the lattice defect of ice seems

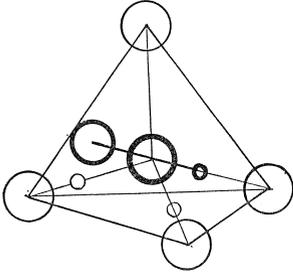


Fig.8 Formation of lattice defect.
KOH is shown by thick lines.

to be produced by the substitution of a KOH molecule for a water molecule as shown in Fig.8, and dispersion A may be ascribed to the orientational polarization of water molecule. As the shape and dimensions of water molecules and their binding forces differ appreciably from most other compounds, the possibility of forming solid solutions in ice was formerly doubtful. Recently, solid solution of NH_4F ,⁽⁸⁾ HF ⁽⁹⁾ or NH_4OH ⁽¹⁰⁾ in ice was admitted for the explanation of the experimental results at temperatures higher than -100°C . On the other hand several investigators⁽¹¹⁾ concluded that crystal growth of ice is poor at temperatures as low as that of liquid air. Therefore in KOH-doped ice we must assume the existence of a very fine microcrystal around each KOH molecule.

When the dielectric measurement was made very slowly during 5 hours while the ice is being cooled from -20°C to -180°C , the result was almost the same as in the case of the measurement in the heating stage of the abruptly frozen ice. The saturation polarization at the concentration of about 0.03N KOH may be explained by assuming the existence of a critical limit for substitution of KOH molecules.

The origin of dispersion B is considered as a superposition of the orientational

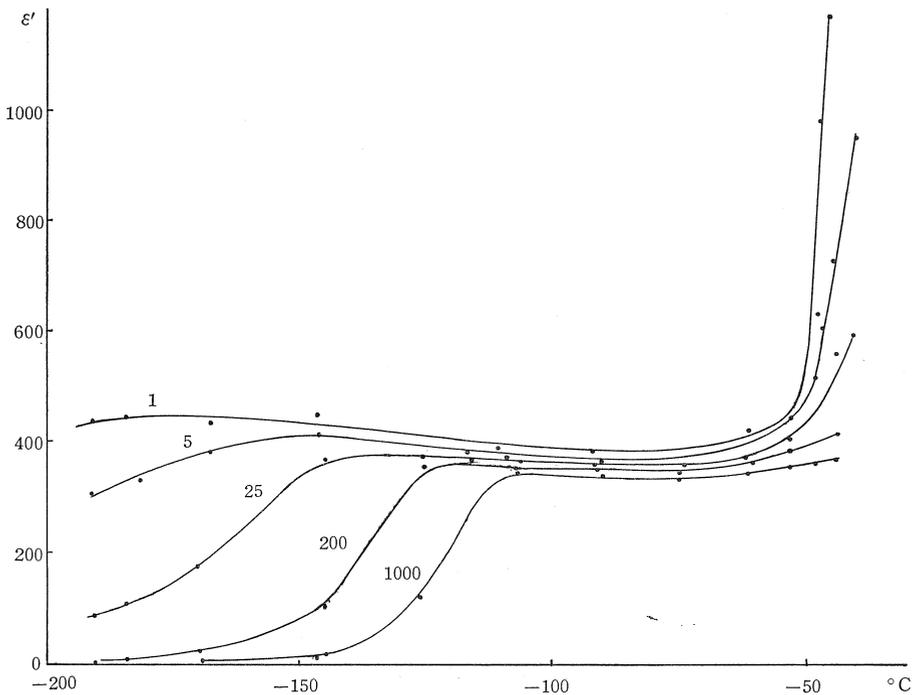


Fig. 9 The temperature dependence of ϵ' of ice doped with 0.1N NaOH.

polarization of ice molecules mentioned above and anomalous space charge polarization due to the impurity.

The temperature dependence of the real part of the dielectric constant of ice doped with 0.1N NaOH and its Cole-Cole diagram at -142°C are shown in Fig. 9 and Fig. 10 respectively, from which we learn that the dielectric dispersion is alike in ice doped with NaOH and KOH. The dielectric dispersion of LiOH-doped ice was also found as in Fig. 11 in a manner somewhat different

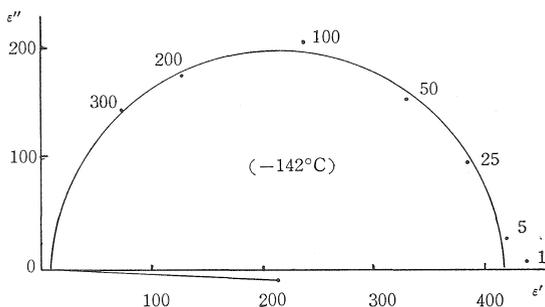


Fig. 10 The Cole-Cole diagram of ice doped with 0.1N NaOH at -142°C

from that of NaOH or KOH-doped ice. This difference may be attributed to that of alkali ion radius. In NH_4OH or $\text{Ba}(\text{OH})_2$ -doped ice the dispersion corresponding to the dispersion B of caustic alkali-doped ice appeared markedly as shown in Fig. 12 and Fig. 13, but the dispersion corresponding to the dispersion A could not be found. Orientational polarization does not seem to occur in these cases, as a NH_4OH molecule can not be substituted for a water molecule on account of the larger radius of NH_4 ion, and $\text{Ba}(\text{OH})_2$ molecule can not do so because of the divalence of Ba atom.

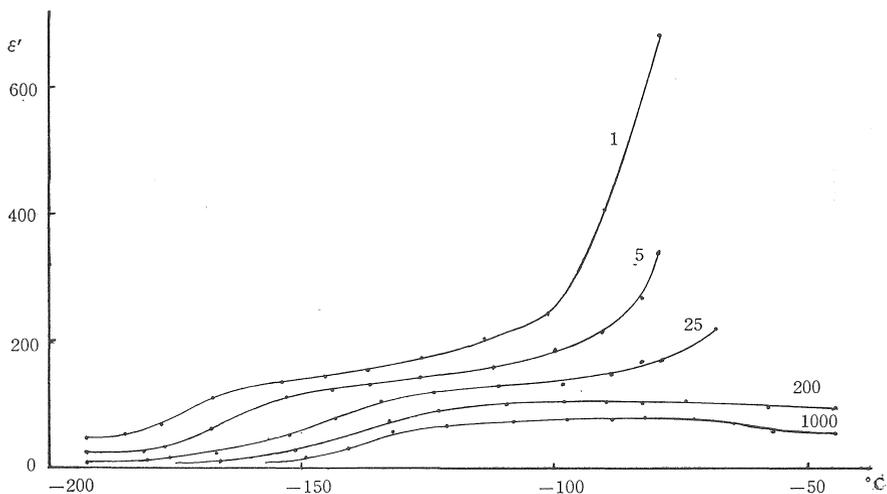


Fig. 11 The temperature dependence of ϵ' of ice doped with 0.5N LiOH.

Other doped ices

On doped ice with 0.1N H_2O_2 a dielectric dispersion occurred at a temperature about -120°C as shown in Fig. 14. The Cole-Cole diagram at -97°C and the temperature dependence of the relaxation time are shown in Fig. 15 and Fig. 16 respectively,

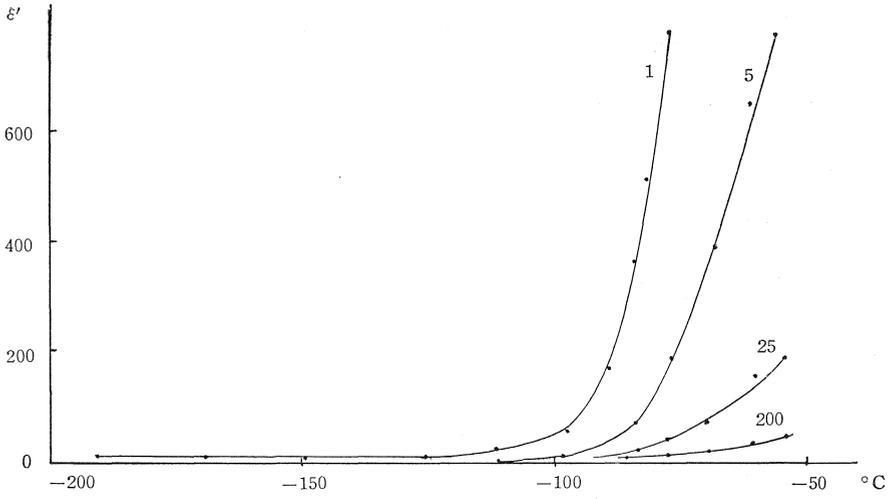


Fig. 12 The temperature dependence of ϵ' of ice doped with 0.1N NH_4OH .

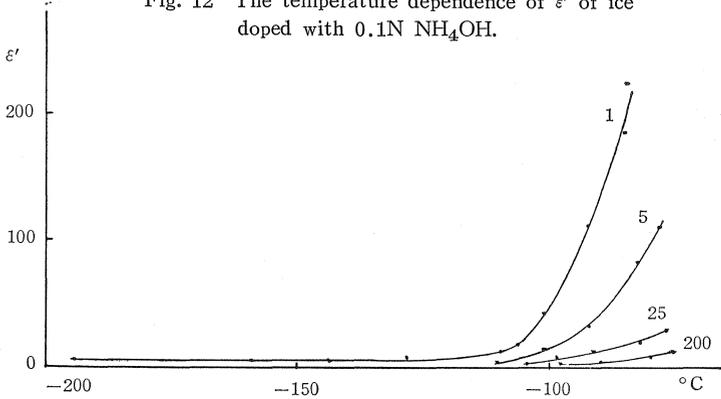


Fig. 13 The temperature dependence of ϵ' of ice doped with 0.001N $\text{Ba}(\text{OH})_2$.

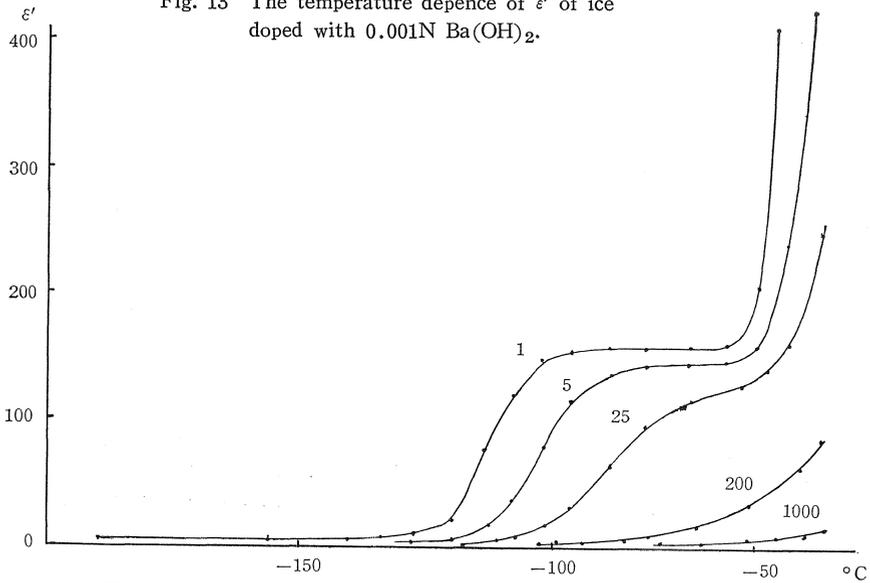


Fig. 14 The temperature dependence of ϵ' of ice doped with 0.1N H_2O_2 .

The activation energies calculated from the curve in Fig. 16 are between 3.6 and 5.8 Kcal/mol. These are slightly larger than the value for KOH-doped ice, but the dielectric dispersion at temperatures below about -70°C may be ascribed to the orientational polarization as mentioned in the caustic alkali-doped ice. Lattice defect of ice is probably produced by the substitution

of one H_2O_2 molecule for two water molecules as shown in Fig. 17.

Dielectric properties of NH_4F -doped ice at temperatures from -65°C to -15°C were investigated by Zaromb and Brill,⁽⁸⁾ who assumed the existence of the solid solution to explain the experimental result. In the present experiment, the dielectric measurement was carried out at temperatures above -180°C as shown in Fig. 18. In this case the dispersion corresponding to the dispersion A of caustic alkali-doped ice appeared, and its activation energy was about 4.6 Kcal/mol, which is nearly equal to the value 4 Kcal/mol obtained by Zaromb and Brill using the frequencies 20 c/s $-$ 600 Kc/s, in the temperature range from -65°C to -15°C .

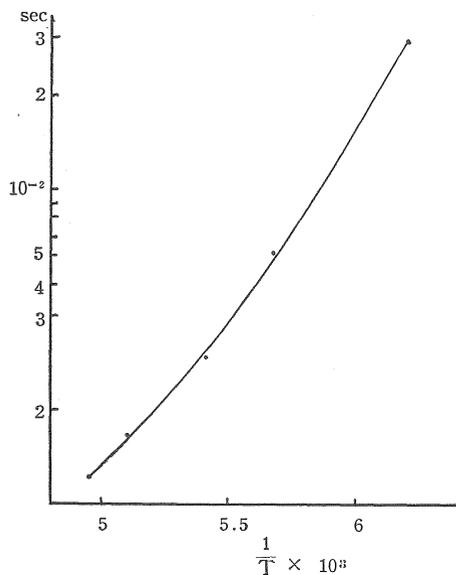


Fig. 16 The temperature dependence of the relaxation time.

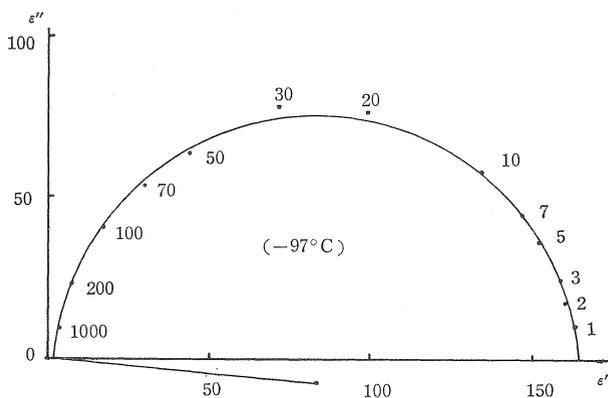


Fig. 15 The Cole-Cole diagram of ice doped with 0.1N H_2O_2 at -97°C .

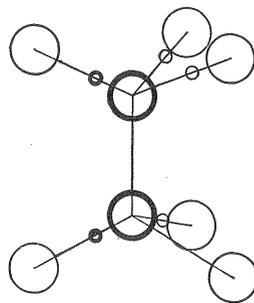


Fig. 17 Formation of lattice defect. H_2O_2 is shown by thick lines.

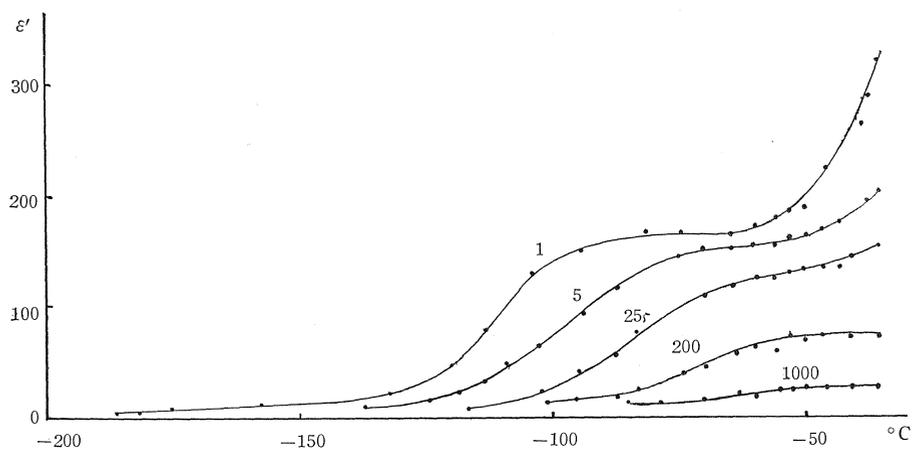


Fig. 18 The temperature dependence of ϵ' of ice doped with 0.5N NH_4F .

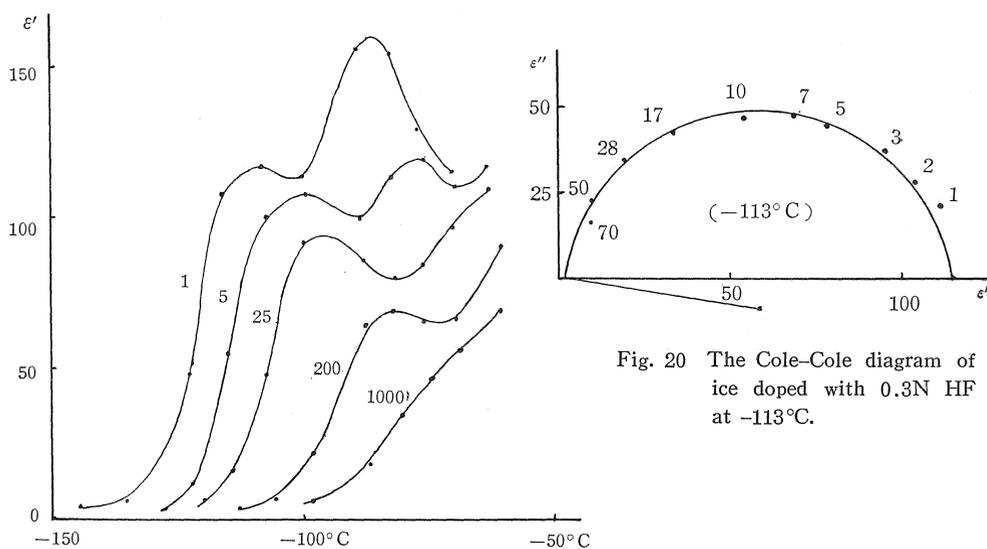


Fig. 19 The temperature dependence of ϵ' of ice doped with 0.3N HF.

Fig. 20 The Cole-Cole diagram of ice doped with 0.3N HF at -113°C .

The dielectric dispersion of HF-doped ice at a higher temperature (-10°C) has been studied in detail by Steinemann⁽⁹⁾ who assumed the growth of the solid solution of ice and HF. In the present experiment at lower temperatures dielectric dispersion as shown in Fig.19 and Fig.20 was obtained.

On HCl or KCl-doped ice dielectric dispersion analogous to that on NH_4OH or $\text{Ba}(\text{OH})_2$ -doped ice was found. The fact that the orientational polarization can not happen at low temperatures seems to be due to the none existence of the lattice defect like that assumed in HF-doped ice.

4. Conclusions

The dielectric dispersion at low temperatures below -100°C , which may be due to the orientational polarization was found only in KOH, NaOH, LiOH, H_2O_2 , NH_4F or HF-doped ice and not in $\text{Ba}(\text{OH})_2$, NH_4OH , HCl or KCl-doped ice, and the reason for this difference has been discussed above.

As to the dielectric measurement of doped ice at the frequency 1 c/s we could not detect any indication of Curie point of ferroelectricity at about 100°K mentioned by Dengel et al, but the possibility of ferroelectricity with a relaxation time of the order of hours must not be denied by the fact. There can be some ferroelectric polarization which is caused by a proton jumping between the O-atoms, of very long relaxation time having no relation to the dielectric behavior found in the present experiment.

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