

Dielectric Low-Frequency Dispersion and Crossover Phenomena of HCl-Doped Ice

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Experimental results for the dielectric measurement of HCl-doped ice are presented. A dielectric low-frequency dispersion was observed at a lower frequency side than the intrinsic Debye dispersion and is discussed on the basis of the temperature dependence of the relaxation time and the dielectric strength. In HCl-doped ice showing crossover phenomena between ac and dc conductivities on temperature dependence, the relaxation time of the low-frequency dispersion is constant above the crossover temperature. It increases with decreasing temperature below the crossover temperature, but HCl-doped ice does not clearly show crossover between relaxation times of the Debye and the low-frequency dispersions on temperature dependence.

Introduction

HF- or HCl-doped ice grown from its dilute aqueous solution shows crossover phenomena,^{1–3} in which the Debye strength has a minimum and high- and low-frequency conductivities for the Debye dispersion cross each other at the crossover temperature. These phenomena have been understood as an exchange of roles between the two types of defects, i.e. DL defects and ionic defects. Jaccard's theory⁴ of the electrical dynamics of the defects in ice assumes dc conductivity caused by minor defects and dielectric dispersion caused by major defects. Generally it has been understood that the dc conductivity is the low-frequency limited conductivity of Debye dispersion. Thus, the defect dynamics gives good explanation for the crossover phenomena as well as the minimum dispersion strength. In their previous paper,³ the authors showed that electric properties of HCl-doped ice can be explained with a dynamics of point defects and conductivity components of point defects (DL and ionic defects) leading to a crossover phenomenon.

On the other hand, experimental results^{5–14} of the frequency dependence of complex dielectric constants in undoped and doped ice show some dielectric dispersions at much lower frequencies. Low-frequency dispersions in undoped ice were found in temperature, time, and pressure dependences,^{7,8} but those in doped ice were found only in temperature dependences.^{9–14} These low-frequency dispersions are considered to be caused by a space charge effect related to proton conduction in ice but have not been understood well. This paper tries to clarify the roles of defects for the low-frequency properties of HCl-doped ice.

Experiment and Results

Single crystals of ice were grown from a dilute aqueous solution of HCl with a modified Bridgman method.¹⁵ The water used was distilled, deionized, and degassed and contained HCl at concentrations below 1×10^{-4} M. The direction of crystal growth was mostly along the *c*-axis, and the growth rate was about 30 mm/day. The size of the obtained single crystals was roughly 35 mm in diameter and 50–100 mm in length, and its dislocation density was as small as 10^6 m^{-2} . Dielectric measurements were made for samples (*c*-plane) with thickness of about 1 mm in a frequency range from 1 mHz to 100 kHz and at temperatures between -10 and -150 °C. Electrodes

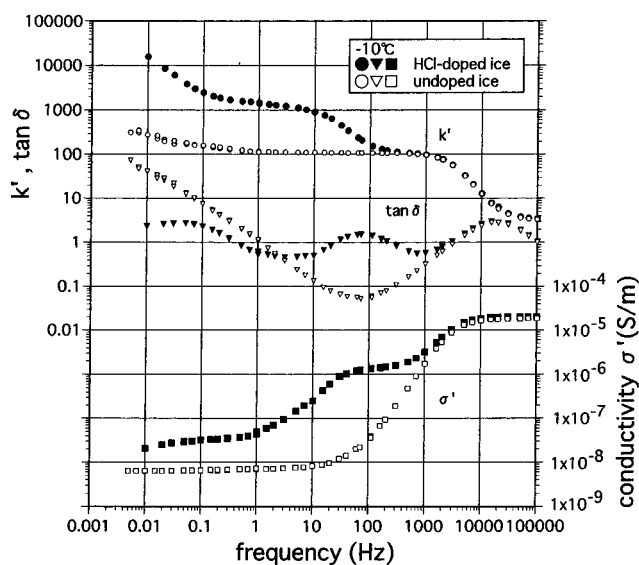


Figure 1. Frequency dependences of the real part of the permittivity k' , dielectric loss tangent $\tan \delta$, and real part of conductivity σ' of undoped and HCl-doped ice at -10 °C. The HCl-doped ice was grown from 1×10^{-5} M HCl solution. The HCl concentration of the sample was estimated as 2.5×10^{-7} M from the dc conductivity.

used were tin metal foils that were not Ohmic electrodes nor perfect blocking. These electrodes probably block protons in ice at the boundary and partly exchange some charges.

Figure 1 shows frequency dependences of the real part of the permittivity, dielectric loss tangent ($\tan \delta$), and conductivity in undoped and HCl-doped ice at -10 °C. This undoped ice shows well-known Debye dispersion around 5 kHz and a flat conductivity profile below 100 Hz, which probably is caused from proton conduction and discharge at electrodes. The HCl-doped ice grown from a mother solution of 10^{-5} M HCl shows another dielectric dispersion around 50 Hz. The concentration of HCl was estimated as 2.5×10^{-7} M from the dc conductivity assuming a mobility of positive ionic defect ($2.7 \times 10^{-8} \text{ m}^2/\text{V s}$).² The relaxation time of the dispersion is dependent on HCl concentration; it decreases with the concentration. In this paper the additional dispersion is called the low-frequency dispersion. The origin of this low-frequency dispersion seems to be space charges often reported in previous works.^{5–14}

Figure 2 shows Cole–Cole plots of HCl-doped ice at temperatures from -10 to -140 °C, which was grown from a

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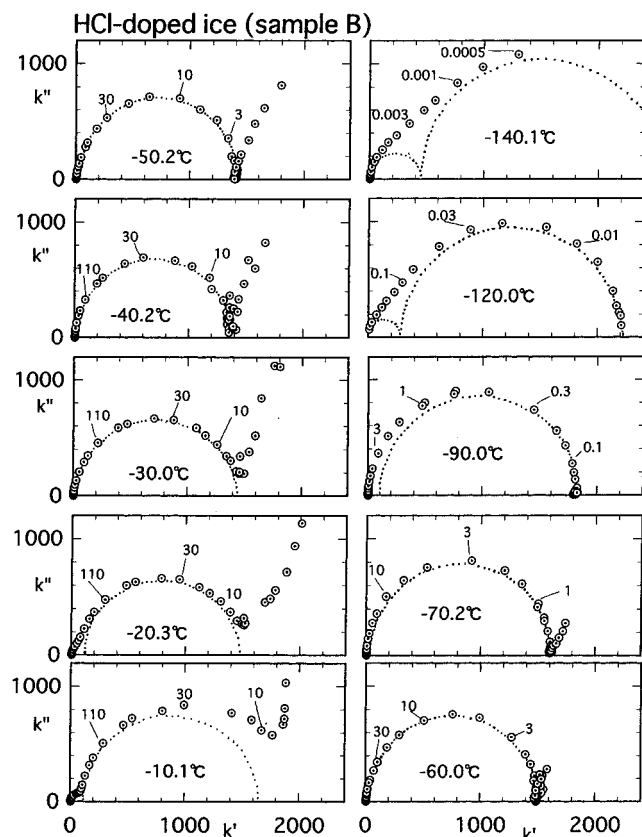


Figure 2. Cole-Cole plots of HCl-doped ice at -10 to -140 °C. The sample was grown from 4×10^{-5} M HCl solution. The HCl concentration was estimated as 6.0×10^{-7} M from the dc conductivity.

mother solution of 4×10^{-5} M HCl concentration. The HCl concentration of the sample was estimated as 6.0×10^{-7} M from the dc conductivity. Data obtained were analyzed using a multidielectric-dispersion model with Cole-Cole's circular arc law. The data analysis of ac and dc conductivities reveals that this sample shows an upper crossover temperature T_{cr} at -39 °C and a lower crossover temperature T'_{cr} at -84 °C.

Above -39 °C the Debye dispersion is gradually absorbed in the low-frequency dispersion with decreasing temperature. The Debye dispersion strength decreases with decreasing temperature. Then the low-frequency dispersion stays in the same frequency range, namely, the relaxation time is constant. Although the data analysis of the low-frequency dispersion in this temperature range is difficult because of an influence from the lower frequency effects, the dielectric strength seems to decrease with decreasing temperature. The Debye dispersion strength showed a minimum around -39 °C (T_{cr}).

At temperatures between T_{cr} (-39 °C) and T'_{cr} (-84 °C) it was rather difficult to distinguish the Debye dispersion from the low-frequency dispersion. It was also noted that the relaxation time of the low-frequency dispersion was constant above the temperature T_{cr} , but below the temperature it varied with temperature.

At temperatures above T_{cr} , the strength of the low-frequency dispersion decreased with decreasing temperature, but below T_{cr} it increased. It is concluded that the Debye and low-frequency dispersions behave similarly in the temperature range and become separated around -120 °C. Below the lower crossover temperature T'_{cr} , the Debye dispersion of HCl-doped ice is clearly separated from the low-frequency dispersion and shows a larger dispersion strength than that of undoped ice at the same temperature.³

The crossover phenomenon of the relaxation time between the low-frequency dispersion and Debye dispersion could not

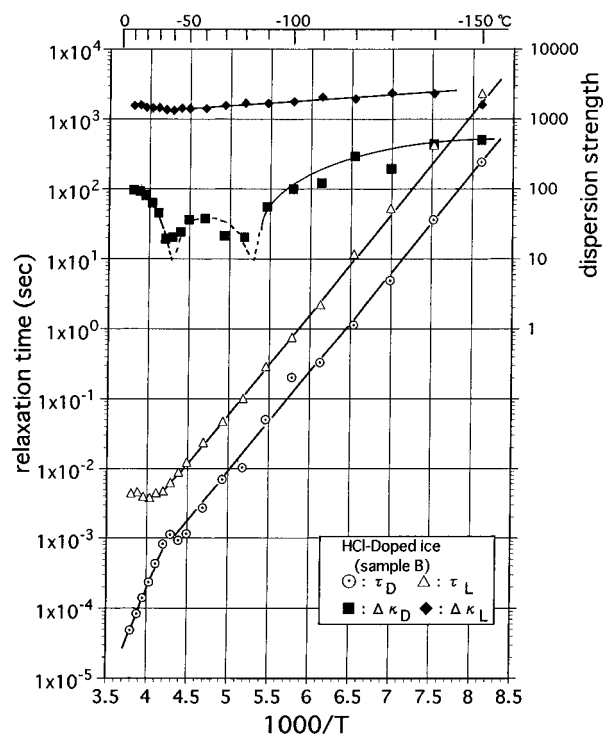


Figure 3. Temperature dependences of relaxation times and dispersion strength of the low-frequency and Debye dispersions of HCl-doped ice. Closed symbols refer to the strength of the low-frequency and Debye dispersions, and the open symbols to the relaxation times. The crossover temperatures are $T_{cr} = -39$ °C and $T'_{cr} = -84$ °C for the Debye dispersion and the ac and dc conductivities. The sample was grown from 4×10^{-5} M HCl solution. The HCl concentration was estimated as 6.0×10^{-7} M from the dc conductivity.

be observed in its temperature dependence as shown in Figure 3. As reported by many researchers,^{5,7,8,10} the dispersion strength and the relaxation time of the low-frequency dispersion became smaller with time.

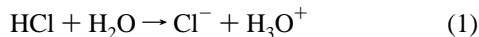
Discussion

The low-frequency dispersion has been observed not only in doped ice but also in undoped ice. The low-frequency dispersion in undoped ice, if the sample is a perfect crystal and the phenomenon is intrinsic, must be observed reproducibly. But that was not the case, and the result was different from sample to sample. The dispersions are considered to be possibly related to crystal imperfections, for example, dislocations. Dislocations in ice crystals are expected to be a source or sink of point defects. Our undoped samples have the low dislocation density of about 10^6 m⁻² and show nonclear low-frequency dispersion in our measuring frequency range. On the other hand, our HCl-doped samples show clear low-frequency dispersion, and the relaxation time depends on HCl concentration. Thus, it can be suggested that this clear low-frequency dispersion is introduced or reinforced by the HCl doping.

In our previous paper,³ we discussed behaviors of the point defects in HCl-doped ice on the basis of the data analysis of ac and dc conductivities. In the same way, the existence of the upper and lower crossover temperatures, T_{cr} and T'_{cr} , means that above T_{cr} thermally activated DL and impurity-introduced L defects are dominant in the electric role and thermally activated ionic and impurity-origin positive defects (H_3O^+ , OH^-) are minor. Between T_{cr} and T'_{cr} the electric role of each defect is exchanged, and below T'_{cr} it is exchanged again. We can assume in our HCl-doped ice below T_{cr} that thermally activated DL and ionic defects can be neglected for the electric role, because the concentration of the former defects decreases rapidly

(0.56 eV) with decreasing temperature as compared to the impurity-origin L defects (0.17 eV)³ and that of the latter is generally smaller than the impurity-origin H₃O⁺ defects. Thus we are only concerned with the thermally activated DL, impurity-origin L, and H₃O⁺ defects above T_{cr} and the impurity-origin L and H₃O⁺ defects below T_{cr} .

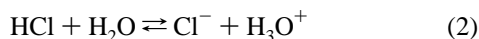
Above T_{cr} the relaxation time of the low-frequency dispersion is constant, and the Debye dispersion is similar to that of undoped ice. The strength of the low-frequency dispersion decreases slightly and that of the Debye dispersion sharply decreases with decreasing temperature. This phenomenon is explained as follows. In this temperature range H₃O⁺ defects are minority carriers and mainly behave in the role of protonic dc conduction. Then H₃O⁺ defects are expected to be perfectly dissociated from HCl at this temperature.³



Since a H₃O⁺ defect has constant mobility and constant concentration that is equal to the HCl concentration doped, the protonic conduction is constant. An equivalent circuit for the dielectric low-frequency process is expected to be a series of resistance and capacitance, since the low-frequency dispersion is a Debye type dispersion. As the geometrical capacity of the sample does not change, we can expect that the constant relaxation time of the low-frequency dispersion is attributed to the constant conduction due to space charge. In our measuring system some discharge of protons around tin electrodes is expected in the high-temperature range. Such a discharge process is not clear. Thus precise data analysis is difficult to give the real strength of the low-frequency dispersion. The decreasing strength of Debye dispersion shows that the dominant electric role of DL defects to orient water molecule dipoles along the electric field decreases with decreasing temperature compared to constant H₃O⁺ defects to reorient dipoles against the electric field.

In the temperature range between T_{cr} and T'_{cr} , the relaxation time of the low-frequency dispersion increases with decreasing temperature. Although an analytical separation of Debye dispersion from the low-frequency dispersion is difficult, the Debye dispersion seems to behave with similar temperature dependence as shown in Figure 3. These relaxation times do not show a crossover of each other at the crossover temperatures T_{cr} and T'_{cr} .

Below T_{cr} , the H₃O⁺ defect undergoes a dissociation–recombination process with Cl[−] ion as follows.



The concentration of H₃O⁺ defects decreases (activation energy 0.31 eV) with decreasing temperature, and the mobility is constant (0 eV).³ On the other hand, thermally activated DL defects become neglected and L defects introduced by HCl doping is constant, and the mobility decreases with decreasing temperature (0.19 eV).³ The contribution for electrical properties is the product of the concentration (n) and mobility (μ).⁴ In this temperature range, the product for L defects is slightly larger than that of H₃O⁺ defects, but the contributions probably have the same order of magnitudes

$$\sigma_+/e_+ \cong \sigma_L/e_L \Rightarrow \mu_+n_+ \cong \mu_Ln_L$$

where σ and e are conductivity and effective charge of defects and subscripts + and L mean H₃O⁺ and L defect respectively. Thus between T_{cr} and T'_{cr} , μ_+ and n_L are constant, and n_+ and μ_L decrease similarly with decreasing temperature. Since the contribution of the two types of defects is the same order of

magnitude, Debye dispersion is not clearly separated and dielectric behavior is determined mainly by protonic dc conduction. Such dc conduction decreases with decreasing temperature, and thus the relaxation time of the low-frequency dispersion as a space charge dispersion increases. This temperature dependence gives an activation energy of 0.28 eV, which is between the dissociation energy of 0.31 eV of H₃O⁺ defect from HCl and an activation energy 0.19 eV of L-defect mobility.

In the temperature range between T_{cr} and T'_{cr} , the low-frequency dispersion behaves as a single Debye-type dispersion, that is, the β factor of Cole–Cole plot is unity, and the dispersion strength increases with decreasing temperature. If the HCl-doped ice is considered to show only protonic dc conduction discussed above, the low-frequency dispersion should be caused from a space charge effect around electrodes. A space charge polarization is generally related to a geometrical capacitance (or bulk permittivity) of the sample and the Debye screening length.^{16,17} The high-frequency permittivity k_∞ , induced from a local electron behavior around water molecules and a deformation of water molecules, decreases with decreasing temperature. Static permittivity k_s of undoped ice increases with decreasing temperature. In this temperature range, the Debye dispersion in HCl-doped ice disappears, but the permittivity of the ice medium, which is induced from a proton behavior in a local area around an oxygen atom of ice lattice, should have the characteristic value ($\cong 100$). The static permittivity k_{Ls} , which is a limiting permittivity to the low-frequency side of the low-frequency dispersion, seems to show a temperature behavior with the Curie–Weiss law ($T_c = 33\text{--}53\text{ K}$). This behavior is similar to the static permittivity k_s of undoped ice (c -plane sample).³ Thus it is expected that the temperature dependence of the low-frequency dispersion is related to the static permittivity k_s .

The following effects have not been understood well: the Debye dispersion in HCl-doped ice below T'_{cr} shows a larger dispersion strength than that in undoped ice, and the relaxation times of the low-frequency and Debye dispersions do not show a crossover.

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