

Dielectric Properties and 110 K Anomalies in KOH- and HCl-Doped Ice Single Crystals

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Dielectric relaxations of HCl- and KOH-highly-doped ice were examined in detail in a wide temperature range. In HCl-doped ice at low temperatures, a relaxation component having a tendency of divergence in the dispersion strength at about 100 K was observed with the activation energy of 0.32 eV, which agreed well with the slow relaxation component in the KOH-doped ice. These are recognized with the component excited by the lattice effect. Detail measurements of the relaxation in KOH-doping revealed (1) freezing of the slow relaxation component and (2) an anomaly which makes a partial phase transition at about 110 K. Using these phenomena, inhomogeneous phases below 72 K in the KOH-doped ice are discussed.

1. Introduction

The issues of a fast dielectric relaxation and a following order–disorder phase transition in KOH-doped ice are strongly interesting phenomena in the physics of ice. The dielectric relaxation time in the fast relaxation was shorter than that of pure ice by as much as 10^7 – 10^8 times at the liquid nitrogen temperature.¹ As for the mechanism of such dramatic shortening, there is a proposal in which the tunneling effect of OH^- is included,² but it has not been elucidated clearly. The fast relaxation branch shows the anomalous temperature dependence. It is observed only below about 210 K, has almost zero activation energy between 210 and 100 K, and below 100 K, is followed by an Arrhenius equation in which the activation energy is about 0.15 eV.³ Moreover, this branch usually splits into two branches below 100 K. It is supposed that these complex behaviors relate to the nonuniformity of the phase XI observed by the neutron diffraction experiment.⁴ The dielectric dispersion spectrum observed in KOH-doped ice consisted of two dispersion branches besides the space charge polarization branch.³ One is the fast relaxation branch and the other the slow one. In their temperature dependence, it was observed that their dispersion strengths changed with correlation and that the dispersion strengths of these two branches irreversibly transfer from the fast to the slow by annealing at high temperatures.⁵

In this report, we discuss the mechanism of fast and slow relaxation branches using observed dielectric dispersion spectra in KOH- and HCl-doped ice and some anomalies observed in the vicinity of 110 K in KOH-doped ice relating to the inhomogeneity in the phase XI.

2. Experimental Section

The dielectric spectrum including the strong space charge polarization was observed in many crystals doped with impurity and even in the pure ice crystals. This space charge is supposed to be responsible for the lattice defects made by impurity or lattice irregularity. This dispersion branch has a long relaxation time distinguished from Debye type components. On the other hand, the Debye type dispersion branch, such as the fast and slow relaxation in KOH-doped ice, is due to point defects substitutionally entered into the lattice point. To increase effectively the latter and measure the dielectric response to the

low-temperature range, the single crystal was grown from the high-concentration liquid of the dopant with the rapid growth method previously mentioned.⁵ The growth rate was 1–3 cm/h, and these crystals uniformly included almost the same concentration of dopant as that of the liquids. The *c*- and *a*-plates were cut from the KOH- and HCl-doped ice single crystal using a band saw and were polished using jig and fine filter paper wetted by a little ethanol. The dielectric dispersion spectrum was measured using a conductance bridge and a loop method in the frequency range from 100 kHz to 10^{-3} Hz. The temperature of the sample was controlled within 0.01 K at each measuring step at the range from just below the melting point to 77 K. Observed dielectric spectra were analyzed using the most least square method aided by a computer program. From these, we obtained temperature dependencies of the dispersion strengths and relaxation times. Especially, in HCl-doped ice, for the sake of subtraction of the space charge component from a total spectrum and of obtaining a reliable Debye component, it was needed to measure in a wide range of the frequency spectrum as accurately as we could.

3. Experimental Results and Discussions

a. Dielectric Relaxation and Curie-Weiss Behavior in HCl-Highly-Doped Ice. Dielectric dispersion spectra were measured in 200 ppm HCl-doped ice single crystals in the temperature range from 200 to 100 K. These spectra included two dispersion branches. One is a Debye, and the other is a space charge polarization. The relaxation time of the Debye component was measured on 10 samples. All of them agreed well with each other. To avoid complexity, data of only four samples, A, B, C, and E, were plotted versus the temperature in Figure 1. The activation energy obtained from the mean was 0.32 ± 0.02 eV. In Figure 1, temperature dependence of the dielectric relaxation time of KOH-doped ice and NH_4F -doped ice are plotted together. As seen in the figure, the dielectric relaxation time of the Debye component in HCl-doped ice, of the slow relaxation (D_2 component) in KOH-doped ice,^{5,6} and of the slow relaxation in NH_4F -doped ice agreed fairly well, and we know that all of these relaxation components are made by the same mechanism. As the L defect formed by HCl-doping is well-expected to be responsible to the dielectric relaxation in HCl-doped ice at low temperatures, all of these relaxations are recognized to be ones which are excited by the L defect. From these approaches, we are able to conclude that the fast relaxation in KOH-doped ice is issued by the action of

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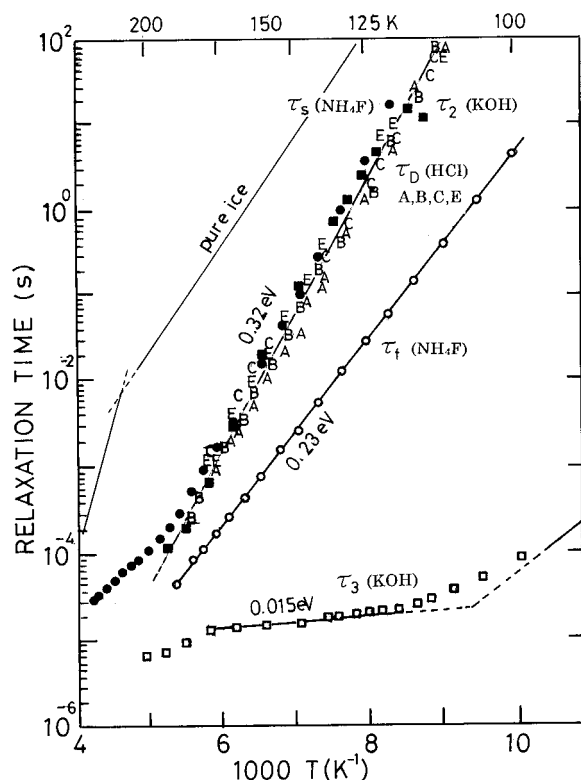


Figure 1. The relaxation times of four HCl-doped samples (denoted by symbols A, B, C, and E) are plotted versus reciprocal temperature together with those of KOH-doped and NH_4F -doped crystals. The three components, i.e. Debye component of HCl-doped ice, D_2 component of KOH-doped ice, and slow component of NH_4F -doped ice, agreed well with each other. These relaxation components have the same mechanism. In the figure, symbols \circ and \bullet , and \square and \blacksquare denote relaxation components in NH_4F -doped ice and KOH-doped ice, respectively.

the OH^- ion. It may be reasonable that two different types of the dielectric relaxation exist in a parallel manner in KOH-doped ice below about 210 K.

As a conclusive remark, in the KOH-doped ice, there are two types of the dielectric relaxation where one of them is of the relaxation by the molecular rotation excited through the action of the L defect, i.e. the D_2 component, and the other is of the relaxation of dipoles through the action of the OH^- ion following the proton shift on the hydrogen bond. At low temperatures, these two mechanisms act in parallel in the lattice of ice, although some kinds of interaction may exist.

The reincrease of the dispersion strength of the Debye component in HCl- and HF-doped ice in the low-temperature range has been reported by several authors,^{7,8} but accurate and reliable data have not been obtained. It was clearly observed in this experiment that the dispersion strength of the Debye component observed in HCl-highly-doped ice followed the Curie–Weiss law below 180 K, with different Curie–Weiss constants from those of pure and KOH-doped ice. The Curie–Weiss temperature was about 90 K which agrees with all samples. But below 120 K, for the sake of elongation of the relaxation time and existence of the space charge polarization, estimation of an accurate Debye component become difficult. If Curie–Weiss behavior is extrapolated, a new phase transition through motion of the molecular rotation may be observed. The measurement of this object has been continued, but a clear phenomena corresponding with phase transition has not been observed. The annealing effect was also observed on the HCl-highly-doped crystal. The annealing of 263 K increases the Debye dispersion strength. By annealing, a number of mol-

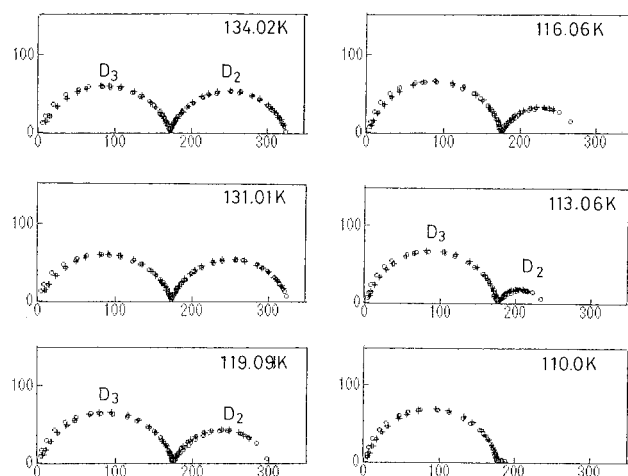


Figure 2. Temperature dependences of the dispersion spectrum and dispersion strength in KOH-doped ice in the vicinity of 100 K. Disappearance of the slow relaxation component (D_2) was observed.

ecules contributed to the Debye component, and then the Curie–Weiss constant increased.

b. Freezing of the Slow (D_2) Component at About 110 K in KOH-Doped Ice. In KOH-doped ice, irrespective to its concentration being high or low, the dielectric relaxation changes its character so that the activation energy changes from about 0 to 0.15 eV. This change of character must be seen in all other properties, especially on the slow relaxation component. We measured the temperature variation of the slow relaxation (D_2) component in the vicinity of 100 K. In a sample, we observed clear disappearance of the D_2 component at about 110 K. In Figure 2, this phenomena was shown on variation of the dispersion spectra at several temperatures and on the temperature change of the dispersion strength.

The disappearance of the D_2 component at about 110 K seems to be followed with an increase of the activation energy in the Arrhenius equation of the fast relaxation. Now, we can consider some links between a possibility of a phase transition in the Debye component in HCl-doped ice which agrees with the D_2 component and freezing of the D_2 component in KOH-doping. Our speculations are as follows. The D_2 relaxation component is issued by the action of the L defect which accelerates the molecular rotation around the OH-axis of the H_2O molecule. In HCl-doped ice at low temperatures, there is a negligible number of defects in natural excitation and a number of the L defects by HCl-doping. On the other hand, in KOH-doped ice, both lattice and OH^- ion act as the defect. These defects make the dipole of the water molecule reorient effectively, and as a result, their excitation interferes with each other by collision on the lattice. Therefore, the excitation of the L defect, in which the relaxation time is very elongated, will be depressed and frozen. Experimentally, the fast relaxation mode excited by the OH^- ion needs the larger activation energy in the lattice in which the D_2 mode froze. Therefore, it is supposed that a low activation energy in the proton shift mode, i.e. D_3 mode, is considered to be brought by the interdependence of the two independent relaxation modes mentioned above. In KOH-highly-doped ice, a remarkable annealing effect in which irreversible transfer from the fast relaxation (D_3) component to the slow relaxation (D_2) component was observed.⁵ By annealing at just below the melting point, the dispersion strength of the slow (D_2) component remarkably increased. That is, the slow relaxation component is a majority and is considerably free from collision with the fast component. We are able to measure the behavior of the L defect in the state similar to HCl-doped ice. As shown in Figure 3, a new relaxation component

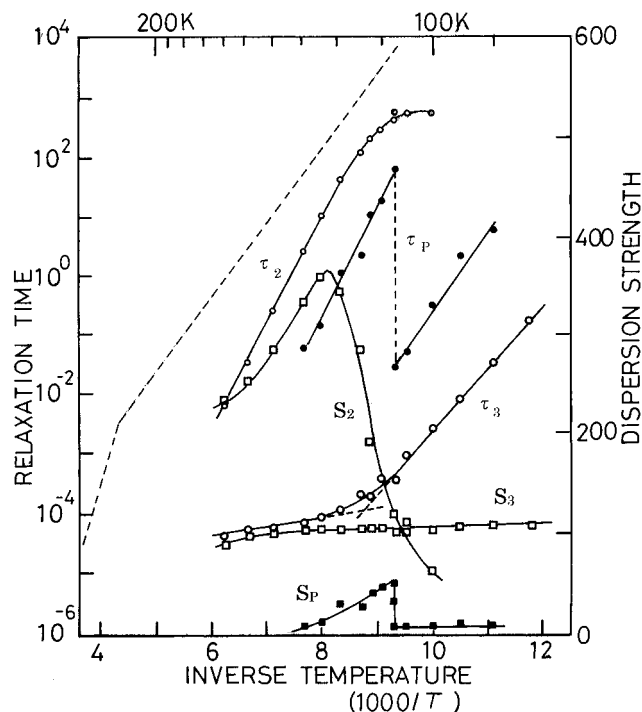


Figure 3. Detail analysis of the dispersion spectrum in KOH-doped ice single crystals. A new relaxation component denoted as "p" component was observed. The "p" component showed some transition-like behaviors in the relaxation time and dispersion strength.

was observed between 80 and 130 K, and its temperature variation of the relaxation time and the dispersion strength were similar to those of well-known phase transitions in ferroelectrics. This behavior corresponds to the phase transition expected in HCl-highly-doped ice, and it may be observed through the shortening of the relaxation time similar to those in the Ih-XI

transition. Therefore, in KOH-doped ice, usually, it is supposed that a part of the relaxation component excited by the L defect freezes and a part transforms to a new symmetry.

4. Conclusive Remarks

The mechanism of two kinds of dielectric relaxation observed in KOH-doped ice was confirmed as those in which the L defect and the OH^- ionic defect excite dipole reorientation independently. The relaxation excited by the L defect, corresponding to the dipole reorientation accompanied with the molecular rotation, is followed (a) by a phase transition when only the L defect is introduced and/or (b) by freezing the molecular rotation when it exists together with the fast relaxation by OH^- . On the other hand, the fast dielectric relaxation, called D_3 , is of a dipole reorientation mode on the hydrogen bond excited by the motion of the ionic OH^- . Below 210 K, this mode becomes stable and observable, and above 110 K, it is excited freely through its low activation energy. Below 110 K, the activation energy by 0.15 eV is necessary because of constraint by freezing of the molecular rotational mode. The crystal becomes dynamically inhomogeneous, because it includes some parts characterized by rotative and nonrotative water molecules before transition to the phase XI. Therefore, the phase transition from Ih to XI will remain incomplete.

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