Deuteron Ordering in KOD-Doped Ice Observed by Neutron Diffraction

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We measured the neutron diffraction of a single crystal of KOD-doped D_2O ice that annealed for 530 h at just below the phase transition temperature $T_c = 76$ K, to investigate the ice Ih to ice XI phase transition (i.e., deuteron disorder to order). We obtained the evidence of the deuteron ordering with annealing: during annealing, the intensity of the 131 diffraction peak in ice XI increased with time and leveled off, which indicated the growth of domains with the deuteron-ordered arrangement. On the basis of the analyses of the change of the diffraction profiles, we estimate the time- and temperature-dependence of the deuteron ordering in ice. The results imply that the ice XI domains in KOD-doped ice increase with increasing time and with increasing temperature up to T_c.

I. Introduction

Ordinary ice (ice Ih) under pressure below about 200 MPa and at temperatures from 0 K to the melting point has the proton-disordered arrangement of which the model was proposed by Pauling[1] and confirmed by neutron diffraction measurements of D_2O ice.[2] The structure of ice Ih is described by the fixed position of oxygen nuclei with a hexagonal arrangement and by the equal distribution of protons (or deuterons for D_2O ice) among the two possible sites on each O−O bond according to the ice rules: (1) there is only one proton on each bond, and (2) there are only two protons close to each oxygen nucleus.

At very low temperatures, an ordered arrangement of protons is likely to become the thermodynamically stable structure. However, the change of water molecule orientations is so slow at low temperatures that thermodynamic equilibrium is not attained over laboratory time scales; as ice Ih is cooled, changes of molecular orientation becomes more and more sluggish, and the crystal eventually becomes "frozen" in a disordered structure.[3]

However, impurity doping can speed the transition to an ordered structure. Kawada[4] measured the temperature dependence of the complex dielectric constant of about 0.1-M KOH-doped polycrystalline ice, and found that the dielectric permittivity of KOH-doped ice becomes very small below about 70 K. Minagawa[5] calculated the static dielectric constant of ice using the Kirkwood-Fröhlich theory and predicted a transition to a proton-ordered phase at about 69 K. Tajima et al.[6] measured the heat capacity of 0.1-M KOH-doped ice Ih: the doped ice was kept at 60−65 K for about 1 week, cooled to 13 K, and then a heat-capacity measurement was started during gradual warming. They found an anomaly at 72 K in the heat-capacity

data, which was not observed in pure ice Ih. On the basis of the analysis of this calorimetric experiment, they proposed that protonic point defects (Bjerrum L- and D-defects) caused by doping with KOH accelerate the reorientation rate of the water molecules, and a phase transition from the proton-disordered arrangement to a proton-ordered arrangement occurs at a transition temperature $T_c = 72$ K in the KOH-doped ice Ih. This ordered ice, which took several days to transform, is named ice XI.[7]

For D_2O ice that is doped with KOD, the transition temperature is at 76 K.[7] Because the neutron cross-section is larger for D than H, it is suitable to study KOD-doped D_2O ice in neutron diffraction experiments. Using the powder diffractmeter at the Institute Laue Langevin, Leadbetter et al.[8] measured the neutron powder diffraction of KOD-doped D_2O ice that was annealed at 65 K and reported that the arrangement of oxygen nuclei in ice XI is the same as that in ice Ih, but the deuterons in ice XI occupy ordered positions such that the spontaneous polarization is parallel to the *c*-axis. Howe and Whitworth[9] measured the neutron diffraction of powdered KOH-doped H_2O ice and confirmed the same structure of the space group $Cmc2_1$ as in Leadbetter et al.[8] Oguro and Whitworth[10] measured the dielectric permittivity and relaxation time for a single-crystal of annealed KOH-doped H_2O ice and showed that a large proportion of the ice is electrically active at 72 K. The depolarization-current study by Jackson and Whitworth[11] also indicates that ice XI is ferroelectric.

Li et al.[12] and Fukazawa et al.[13−16] measured the inelastic neutron scattering (IINS) spectra of KOH-doped ice, and showed that the librational vibrations (hindered rotations of water molecules) in ice XI are clearly different from those in ice Ih. Su et al.[17] measured the vibrational spectra of the ferroelectric ice, and analyzed the vibrations of OH stretching in the proton-ordered ice. Itoh et al.[18,19] did molecular dynamics (MD) simulations and showed that the difference of the vibrational spectra between ice XI and Ih is due to proton ordering along the *c*-axis.

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Line and Whitworth[20] measured the lattice parameter of the KOD-doped polycrystalline D_2O ice as a function of temperature using a high-resolution neutron diffractometer. They demonstrated that the deuteron-ordered structure of ice XI at 5 K has a different *c*-parameter from that of pure ice Ih, and showed that ice XI is orthorhombic. Furthermore, they reported that the transformed ice sample is a mixture of the deuteron-ordered structure (ice XI) and the deuteron-disordered structure (ice Ih). Jackson et al.[21] reported that the neutron diffraction profile for a single-crystal of KOH- and KOD-doped H_2O and D_2O ice, which was annealed for 4.5 days at 70 K, has the 131 diffraction peak at 2.13 Å that is forbidden in ice Ih. By analyzing the peak intensities, they determined that the order parameter η (the ratio of the volume of ice XI to that of the doped ice) is 0.37.

To investigate the process of the deuteron ordering in the slow phase transition from ice Ih to ice XI, we measured the neutron diffraction of a single crystal of KOD-doped D_2O ice that annealed for about 1 week at 62 and 68 K (i.e., just below $T_c = 76$ K). On the basis of analyses of the time- and temperature-dependence of the diffraction profiles, we discuss a change of the deuteron arrangement in ice.

II. Experimental Section

The sample was a single crystal of D_2O ice Ih that was grown from 0.1-M KOD solution using a modified Bridgman technique.[10] A column sample (18 mm diameter, 80 mm length) was cut from the crystal and then placed in an aluminum cell inside a top-loading cryostat of 20 K. To transform ice Ih into ice XI, the temperature of the sample T was warmed to 62 K and kept at 62 K for 530 h. Starting from the time the temperature reached 62 K, we measured single-crystal neutron diffraction profiles for the angle corresponding to the 131 Bragg reflection from the sample in the range of lattice-plane spacings d from 0.8 to 2.8 Å. Measurements were done on the MAX time-of-flight diffractometer in the KENS neutron facility on the pulsed-neutron source in the High Energy Accelerator Research Organization (KEK) in Japan. Each profile required 1 h of exposure to the neutron beam, and 100 profiles were obtained during the 520 h measurement period at 62 K. After the measurements at $T = 62$ K, the sample was warmed to 180 K. We measured the neutron diffraction of the sample at 180 K and confirmed that the deuterons became completely disordered. Then, we repeated the phase transition measurements by cooling back down to 20 K and raising the temperature to the diffraction-measurement temperature of 68 K for 88 h. Finally, we repeated the same step for diffraction measurements at 51 K for 40 h.

III. Results

Figure 1 shows the single-crystal neutron diffraction profiles for the angle corresponding to the 131 Bragg reflection from the KOD-doped D_2O ice at 62 K. The profiles were obtained at $t = 0, 10, 30, 50,$ and 80 h, where t is the duration that the sample was kept at 62 K. All profiles have a large peak at 1.07 Å of the 262 diffraction peak. The 262 peak is observed in the profile of ice Ih with deuteron-disorder. The profile at $t = 0$ does not have any peak outside the 262 peak, but the profile at $t = 10$ h has a weak peak at 2.13 Å of the 131 peak. Jackson et al.[21] showed that the 131 peak is forbidden in ice Ih because it is produced by the deuteron-ordered structure of $Cmc2_1$. The profiles at $t = 30, 50,$ and 80 h also have the 131 peak at 2.13 Å. The integrated intensity of the 131 peak increases with t; for example, the intensity of the 131 peak at 80 h is about three times as large as that at 10 h.
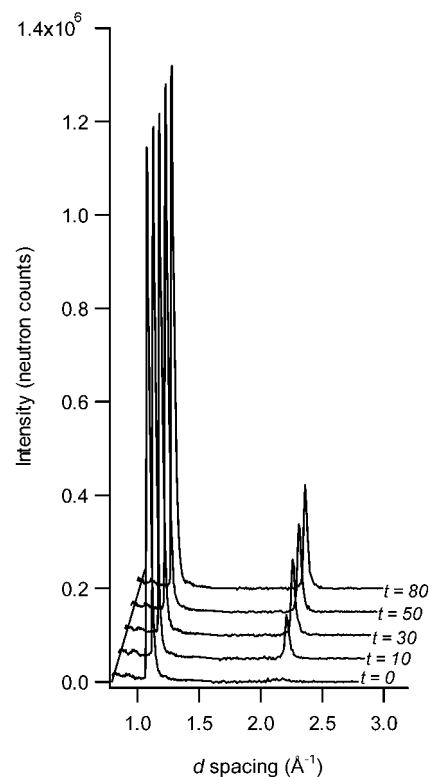
Figure 1. The single-crystal neutron diffraction profiles for the angle corresponding to the 131 Bragg reflection from KOD-doped D_2O ice at 62 K. The profiles were measured at times $t = 0, 10, 30, 50,$ and 80 h starting from when the sample reached a temperature of 62 K after being warmed from 20 K. The peaks of 262 and 131 peaks are observed at 1.07 and 2.13 Å, respectively.
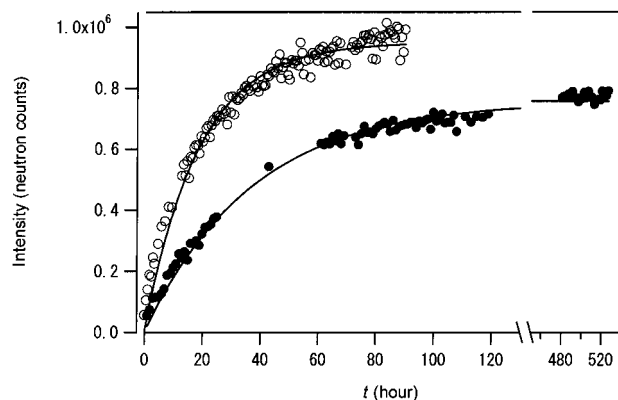
Figure 2. Time dependence of the intensity $I(t)$. Solid circles are from the sample at 62 K, and open circles are for 68 K. Solid lines show the fitted line to $I(t) = C\{1 - \exp(-Jt)\}$, where $C = 7.57 \times 10^5$ and $J = 0.0268$ h^{-1} for $T = 62$ K, and $C = 9.51 \times 10^5$ and $J = 0.0537$ h^{-1} for $T = 68$ K.

The intensity of the 131 peak at 62 K is plotted as solid circle against t in Figure 2. The intensity increases with time until 100 h and then gradually levels off. The intensity of the 131 peak increases with the volume of the deuteron-ordered ice XI phase; therefore, the result indicates that the volume of XI ice rapidly increased just after the ice warmed to 62 K, and then the volume increased slowly. After about 100 h, the volume of ice XI becomes practically constant.

To investigate the temperature effect on the time evolution of the 131 peak, we measured the diffraction profiles of ice that had been kept at $T = 68$ K for $t = 88$ h. All profiles at $T = 68$ K also had the 262 peak. The profile at $t = 0$ did not have any peak outside the 262 peak, but the 131 peak was

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observed in the 1-h profile and thereafter. As shown as open circles in Figure 2, the intensity of the 131 peak increases with time up to 88 h. The intensity and rate of intensity increase for $T = 68$ K is larger than those for $T = 62$ K. Thus, the volume of ice XI with the deuteron-ordered structure in the KOD-doped ice is larger at 68 K than that at 62 K.

We also measured the diffraction profiles in $d = 0.8–2.8$ Å of ice that was kept at 51 K for 40 h. All profiles have the 262 peak, but the 131 peak was not observed in the profiles at $t > 0$. This result implies that the phase transition from ice Ih to ice XI does not take place at 51 K. Thus, the deuterons in the ice were ordered at just below T_c but were not ordered at 51 K.

IV. Discussion

We obtained the changes of the intensity of the 131 peak with t due to the deuteron ordering (Figure 2). The increasing deuteron ordering with increasing t is considered to be due to nucleation of ice XI with the deuteron-ordered arrangement, caused by a deuteronic defect in the KOD-doped ice. Thus, the intensity of the 131 peak can be written $I(t) = C\, P(t)$, where C is the intensity of 131 peak at $t = \infty$ and $P(t)$ is nucleation probability distribution. According to the nucleation theory for a phase transition from a disordered state to an ordered state, $P(t)$ can be expressed by a nucleation rate J and an onset time of nucleation τ_0.[22] Thus,

$$I(t) = C\,[1 - \exp\{-J(t - \tau_0)\}] \tag{1}$$

The data for $T = 62$ K are fitted to $I(t)$ as shown by the solid line in Figure 2, where $C = 7.57 \times 10^5$, $J = 0.0268$ h^{-1}, and $\tau_0 = 0$ h. The theoretical solid line is in good agreement with the measured $I(t)$ for $T = 62$ K. This agreement shows that the onset time of nucleation of the domain of ice XI with the deuteron-ordered structure is short, but the nucleation rate of the domain is very slow. Since the change of water molecule orientation is sluggish at $T = 62$ K, the nucleation rate of the ordered domain is very slow.

For the 68-K data, the theoretical fit to $I(t)$ is shown in Figure 2, where $C = 9.51 \times 10^5$, $J = 0.0537$ h^{-1}, and $\tau_0 = 0$ h, and the line is also in good agreement with the measured values of $I(t)$ for $T = 68$ K. There is no discernible onset time of nucleation at both 62 and 68 K, but the nucleation rate is larger at 68 K than that of 62 K; thus, the growth rate of total volume of ice XI is higher at the higher temperature. This means that there are more nucleation sites for ice XI at higher temperature, and that ice Ih transforms faster into ice XI at higher temperature.

The intensity ratio of the 262 peak to the 131 peak from the sample that was annealed for 80 h at 62 K is 0.316, as shown in Figure 1. According to the structure factor of ice Ih and XI,[21] we calculated that η of the sample is 0.335. This value nearly equals that reported in a previous study.[21] From the intensity ratio of the 262 peak to the 131 peak and eq 1, we obtained η of the ice at $T = 62$ and 68 K as a function of t, as follows:

$$\eta = c\{1 - \exp(-Jt)\} \tag{2}$$

where c is the value of η at $t = \infty$. At 62 K, $c = 0.382$, whereas $c = 0.479$ at 68 K. Equation 2 shows that the deuterons are partially ordered in the KOD-doped ice, even at $t = \infty$. Furthermore, η for $T = 68$ K is higher than that at 62 K; hence, η depends on both time and temperature.

Deuteronic defects created by KOD probably generate domains with the deuteron-ordered arrangement. Suga [23] roughly estimated, on the basis of results of extrapolation of the relaxational heat capacity of ice annealed for 624 h, that proton ordering in pure ice requires about 10^6 years. Furthermore, the partial proton-ordering is also observed in thin layers of pure ice.[17] Because the change of water molecule orientation in the thin film of ice is so much faster than that of bulk ice, the phase transition from ice Ih to ice XI can take place in laboratory time scales. These results strongly suggest the existence of the proton ordering in a pure ice crystal, which has been kept for a long period of time at low temperature. Thus, natural ice on the satellite of the outer planets and comets may have the proton-ordered arrangements. This implies the existence of the electricity produced by the ordered ice on the surface of the planets, because ice XI is ferroelectric.

In our experiments, there were domains of ice XI with the deuteron-ordered arrangement. The domains probably exist around the KOD that was incorporated into the ice lattice. If the deuteronic defects are isolated, this 0.1-M doping would have an average distance of 5.7 nm between defects. Assuming that the domains are spherical, the volume ratio between the deuteron-ordered and disordered phases is 0.524. Thus, the KOD-doped ice has small, deuteron-ordered domains at 62 and 68 K, and then the size of domains increases with t. Finally, the diameter of the domain becomes about 5.7 nm.

These values of η are lower than that calculated from the heat capacity data,[7] but higher than those observed in the thin film of pure ice.[17] The analyses, which explain why a fully proton-ordered ice does not exist, are very important for understanding the dynamics of protons in ice and water, and occurrence of ice in the universe. To investigate the proton ordering and the proton-ordered domains, the observation of the structure and the dynamics of ice and water in nanoscale is important.

V. Conclusions

We have reported the time- and temperature-dependence of the intensity of the 131 neutron-diffraction peak of a single crystal of KOD-doped D_2O ice. The measurements were made as the crystals annealed for about 1 week at 62 and 68 K, which is just below the phase transition temperature $T_c = 76$ K. We found that the intensity of the 131 diffraction peak, which is due to the deuteron-ordered phase, increased with time and leveled off after about 5 days at 62 K. The rate that the 131 diffraction peak increased was greater at 68 K. The diffraction data were consistent with relatively rapid nucleation of ice XI followed by relatively slow growth of this deuteron-ordered phase. We estimated the time- and temperature-dependence of the order parameter in the ice, and thus inferred the change of the deuteron-ordered domains with time and temperature. The results imply that the KOD-doped ice has the deuteron-ordered domains just below T_c, and the size of domains increases with time and temperature.

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