論文内容の要旨

Hydrogen ordering in ice observed from neutron diffraction and infrared spectroscopy
（中性子回折及び赤外分光法を用いた氷の水素秩序化の研究）

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Laboratory experiments and infrared observations suggest that most water ice exists in a crystalline phase in our solar system. At ambient pressure, crystalline ice has two kinds of structure, which are ordinary ice Ih with disordered hydrogen atoms and ice XI with ordered hydrogen atoms. Ice XI is considered to be thermodynamically stable at low temperatures and, ice XI has been prepared for potassium hydroxide-doped ices in laboratories. The dopant acts as a catalyst for the phase transition from ice Ih to ice XI. For deuterium-substituted ice (D_2O), nucleation of ice XI occurs below 65 K, and growth occurs 60–74 K. Ice XI rapidly transforms back to ice Ih when the ice is kept at temperatures higher than 76 K.

The existence of hydrogen-ordered ice in space is the subject of continuing astronomical debate because ice XI is ferroelectric. Electrostatic forces, caused by the ferroelectricity, increase the sticking probability of icy grains, and might play an important role in grain evolution in space. To discuss the existence of hydrogen-ordered ice in space, we need to investigate the kinetics and formation process of ice XI. For precise understanding of nucleation and growth process of ice XI, I performed neutron diffraction measurements of deuterium-substituted LiOD, NaOD, KOD, DCl, ND_3, and $Ca(OD)_2$-doped ices, and investigated how the temperature history, kind of the dopant and concentration of the dopant affect ice XI formation.

Formation of ice XI was observed in LiOD and NaOD-doped ices besides KOD-doped ices. Rietveld analysis was carried out to obtain structure parameters of ice XI. The structure parameters of ice XI in LiOD- and NaOD-doped ices were obtained for the first time in this study, and were the same as that in KOD-doped ice within the error. The mass fractions of ice XI (*f*) were also obtained using Rietveld analysis. The lager *f* value was obtained from the lower concentration of the dopant although formation of ice XI did not occurred in the 0.0001 M KOD-doped ice and pure ice.

I measured neutron diffraction patterns of 0.013 M KOD-doped ice to investigate the influence of temperature histories. The doped ice Ih transformed to ice XI after annealing at 57 and subsequently at 68 K The *f* value of the doped ice, which had once experienced being ice XI (f = 0.23 ± 0.02), was larger than that of the doped ice, which had never experienced being ice XI (f = 0.14 ± 0.01). Results propose a thesis that small hydrogen-ordered domains remained in the ice Ih, which had once transformed to ice XI, and accelerated the phase transition from ice Ih to ice XI.

To understand this phenomenon in detail, I performed time-resolved neutron diffraction measurements on 0.1 M NaOD-doped ices, and investigated whether formation of ice XI occurs at temperatures above 65 K, which is out of the nucleation temperatures. Formation of ice XI occurred at 70 and 72 K when the ice had experience being ice XI in the past. This result suggests the presence of a template acting as the nuclei of ice XI. Thus, small domains with ordered hydrogen, which cannot be detected with neutron diffraction, can exist above the boundary temperature between ice Ih and XI. The small ordered-domain is called “memory” of hydrogen ordered structure because of the residual structure of ice XI. In the previous studies, ferroelectric hydrogen-ordered ice is considered to exist in the very narrow temperature range, but our experiments show a possibility that the hydrogen ordered ice exists in wider area in space.

To obtain direct evidence of existence of ice XI in space, it is necessary to understand the feature of infrared spectra of ice XI as standard data for astronomical infrared observations. In this study, I measured IR spectra of KOH-doped film ice to investigate spectral changes caused by hydrogen ordering. Infrared absorption spectra of ice were obtained at 4, 60, 100, 140, 160, and 240 K. In each spectrum, a broad peak was observed at around 850 cm^{-1}, which is derived from libration of water molecules. The full width at half-maximum of the librational peaks was notably narrower at temperatures less than 140 K. These results suggest that ice at temperatures less than 140 K has partially ordered hydrogen. These results are consistent with the fact that hydrogen ordering in film ice occurs below 150 K. Our results demonstrate that hydrogen-ordered ice in space is detectable using infrared telescopes in the near future.

In this thesis, I also discuss hydrogen ordering in ice at high pressure using neutron diffraction experiments. Our results indicate that hydrogen-ordered structure of high-pressure ice VI is ferroelectric. Hydrogen-ordered ferroelectric ices might exist not only in icy grains and icy bodies’ surface, but also in icy bodies’ interior.