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NEUTRON SCATTERING MEASUREMENTS ON VOSTOK ANTARCTIC ICE

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Abstract: We measured the incoherent inelastic neutron scattering (IINS) of Vostok Antarctic ice in order to investigate the arrangement of protons in the ice and to verify the proton ordering in Antarctic ice previously observed by IINS measurements on Dome Fuji Antarctic ice (FUKAZAWA *et al.*, Chem. Phys. Lett., **294**, 554, 1998a). The IINS spectrum of Vostok ice at 500 m in depth has a peak at 19 meV in the region of translational lattice vibrations, while the peak in Vostok ice at 2452 m in depth is much lower. Ice XI with a proton-ordered arrangement has a sharp peak at 19 meV, while ordinary ice (ice Ih) with a proton-disordered arrangement does not have such a peak. These results of analysis of the IINS spectra indicate that Vostok ice at 500 m in depth has a proton-ordered arrangement.

1. Introduction

Ice Ih is an ordinary ice, and the oxygen nuclei of water molecules have a hexagonal arrangement. Ice Ih under pressure below about 200 MPa and at temperatures from 0 K to the melting point has a proton-disordered arrangement of which the model was proposed by PAULING (1935) and confirmed by neutron diffraction measurement of D_2O ice (PETERSON and LEVY, 1957). As shown in Fig. 1A, the proton arrangement in ice Ih is described by the equal distribution of protons 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. Since the pressure in the Antarctic ice sheet does not exceed 50 MPa, Antarctic ice was considered to be ice Ih with a proton-disordered arrangement.

0.01 mole KOH-doped ice has ice XI below 72 K (TAJIMA *et al.*, 1982) of which the oxygen nucleus structure is the same as that of ice Ih, but protons occupy ordered positions on O-O bonds. LEADBETTER *et al.* (1985) and LINE and WHITWORTH (1996) measured the neutron diffraction of powdered ice XI and obtained the ferroelectric structure of the space group $Cmc2_1$, as shown in Fig. 1B. JACKSON *et al.* (1997) also obtained the same result in a neutron diffraction study of a single-crystal of ice XI. These results showed that protons in ice Ih are equally distributed among the two possible sites on each O-O bond, while protons in ice XI are fixed at one site on each O-O

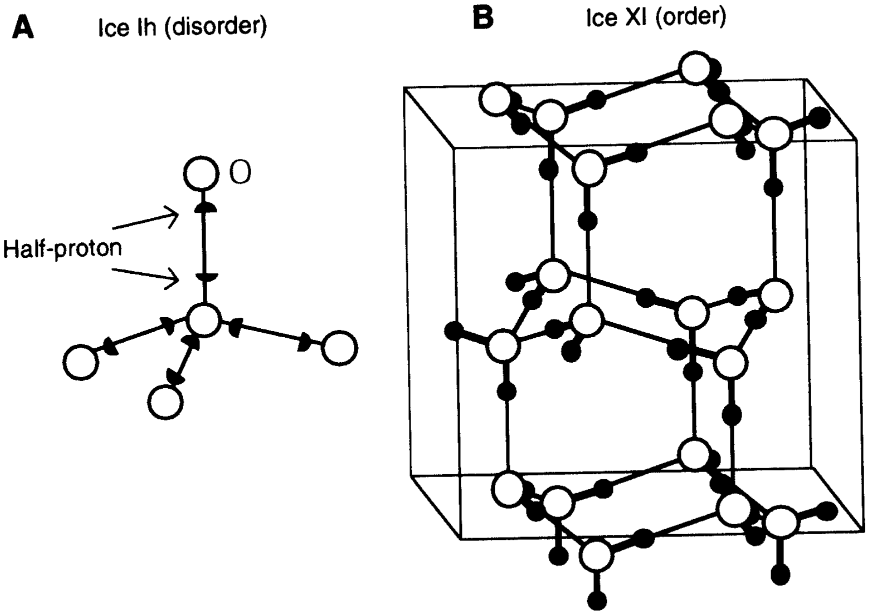

Fig. 1. (A) Location of protons in ice Ih as determined by the neutron diffraction pattern (PETERSON and LEVY, 1957). Oxygen nuclei are represented by open circles and protons by shaded half-circles. There are two half-protons along each O-O axis. (B) Structure of ice XI (space group is $Cmc2_1$) as determined by the neutron diffraction pattern (LEADBETTER et al., 1985). Open circles represent oxygen nuclei and shaded circles represent protons.

bond. SUGA (1985) roughly estimated, on the basis of results of extrapolation of the relaxational heat capacity of ice annealed for 624 hours, that the phase transition from pure ice Ih to ice XI requires about 10^6 years.

FUKAZAWA *et al.* (1998a) measured the incoherent inelastic neutron scattering (IINS) spectra of Dome Fuji (DF) ice retrieved from the Antarctic ice sheet, because DF ice has been kept at a constant temperature for a long period (about 10^4 years) in the polar ice sheet. They hypothesized that there is a very slow change in the proton arrangement in ice. They found that DF ice at a depth of 201 m has a sharp peak of librational vibration. Furthermore, FUKAZAWA *et al.* (1998a, b) measured the IINS spectra of ice XI with a proton-ordered arrangement and ice Ih with a proton-disordered arrangement, and they compared the spectra of DF ice, ice XI and ice Ih. The results showed that the librational vibrations of DF ice (at a depth of 201 m) are remarkably similar to those of ice XI, while the librational vibrations of both DF ice (at a depth of 201 m) and ice XI are clearly different from those of ice Ih. Based on the results of IINS measurements and analyses of the Raman spectra of the translational lattice vibrations in DF and other polar ice, FUKAZAWA *et al.* (1998a) proposed that Antarctic ice in the area where $T_i \leq 237\,K$ (T_i: ice temperature) contains a proton-ordered arrangement. The T_i dependence of the ratio of ordered protons obtained by analysis of IINS and Raman spectra in Antarctic ice is consistent with the Landau theory of second-order phase-transition at $T_i = 237\,K$ (LANDAU and LIFSHITZ, 1959).

Vostok ice (from 290 to 1950 m in depth) recovered from the Antarctic ice sheet

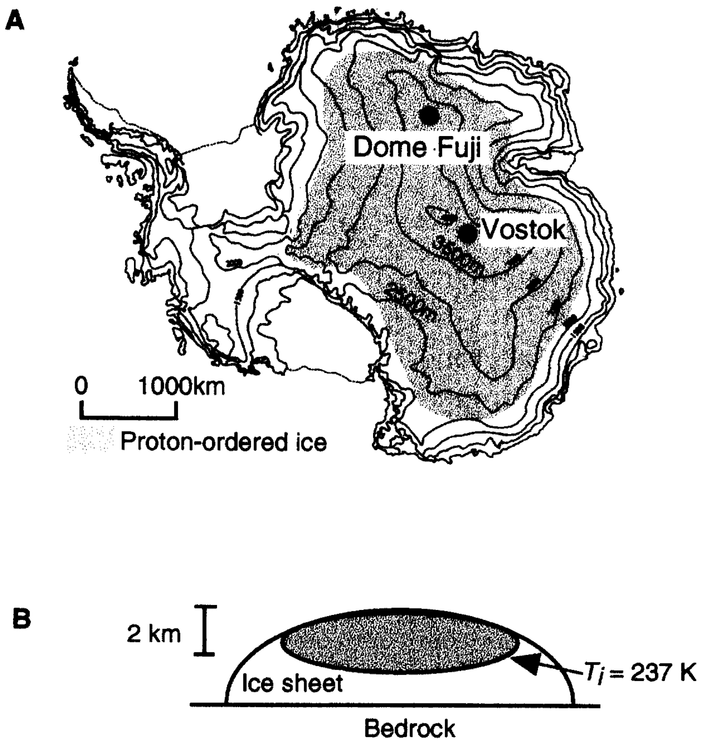

Fig. 2. (A) The drilling sites of Vostok ice (78°28′S, 106°49′E) and Dome-Fuji ice (77°22′S, 39°37′E) in Antarctica. The hatched area shows the area in the ice sheet surface where $T_i \leq 237$ K. (B) Schematic diagram of a cross section of the Antarctic ice sheet. The hatched area shows the area where $T_i \leq 237$ K.

(Fig. 2) has remained for a long period of time (about 10^4 years) at T_i below 237 K. For instance, T_i of the ice at a depth of 500 m is 219 K while that at 2452 m is 245 K. Furthermore, FUKAZAWA *et al.* (1996) measured the Raman spectra of Vostok ice at depths from 500 to 2452 m, and reported that the translational lattice vibrations at 500 m in depth are clearly different from those at 2452 m in depth. Thus, Vostok ice at a depth of 500 m is thought to have a proton-ordered arrangement. In order to investigate the proton arrangement in Vostok ice, we measured the IINS of Vostok ice at depths of 500 and 2452 m. In this paper, we report the results of analyses of the IINS spectra in Vostok ice.

2. Experiment

We measured the IINS spectra of Vostok ice at depths of 500 m (T_i=219 K) and 2452 m (T_i=245 K) by using a crystal-analyzer time-of-flight (CAT) spectrometer on a pulsed spallation neutron source at the High Energy Accelerator Research Organization (KEK), Japan. In the CAT spectrometer, the scattering angle (θ) is about 0° for energy of $\geq$20 meV (IKEDA and WATANABE, 1984) and it is lower than that in the incoherent neutron chopper (INC) spectrometer used for the measurement of librational vibrations in DF ice (FUKAZAWA *et al.*, 1998a). In order to avoid multiple scattering from the sample, thin-plate samples (30×100 mm, 0.4-mm thick) were cut from ice cores, with the plate surface being parallel to the vertical direction of the core. The samples (polycrystalline) were placed in a flat-plate aluminum cell, and the incident beam direction was perpendicular to the plate surface. The spectra were measured at 21 K.

3. Results

Figure 3A and B show the spectra (0–130 meV) of Vostok ice at depths of 500 and 2452 m. In the range of 50–130 meV, the spectra of Vostok ice at 500 and 2452 m in depth have a peak at 71 meV that spread from 51 to 118 meV. This peak is also found in the spectra of ordinary ice (artificial ice; ice Ih), measured by Klug *et al.* (1991) and

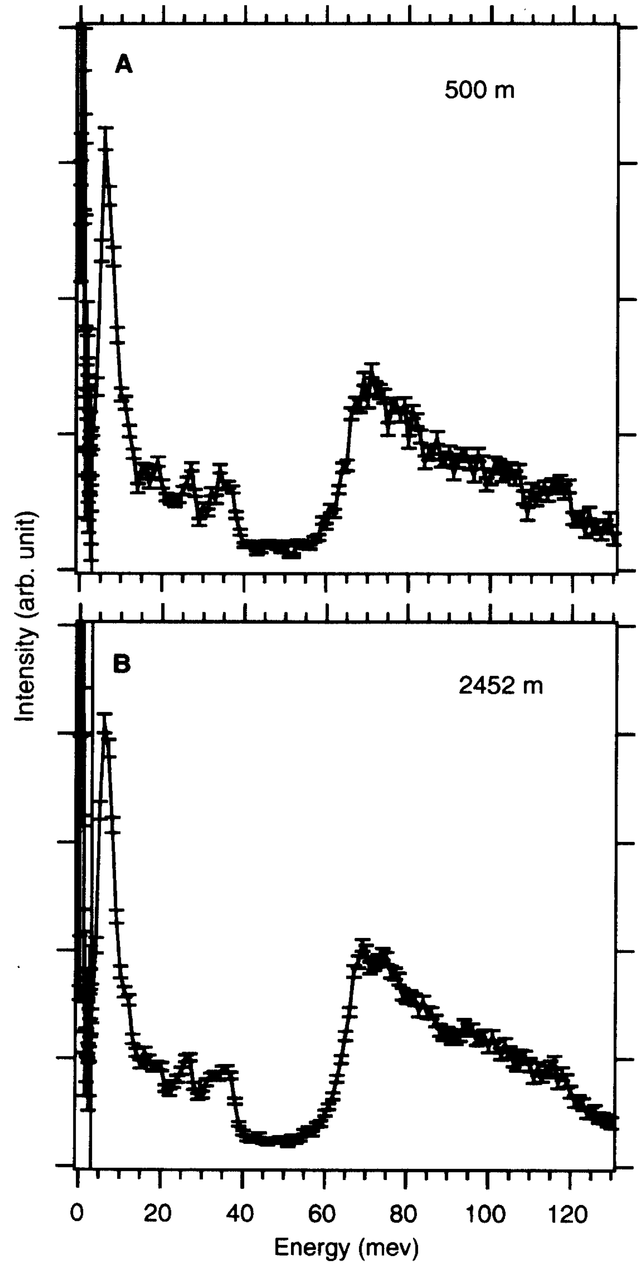

Fig. 3. IINS spectra from Vostok ice at depths of 500 m (A) and 2452 m (B). The intensities of the spectra were normalized by the integrated intensities of elastic scattering.

LI and Ross (1992), and is assigned to librational vibrations of water molecules. The spectra have a small peak at 97 meV, which is broad and cut off at 118 meV. The boundary between the peaks at 71 and 97 meV is located at approximately 88 meV.

The spectra of Vostok ice at depths of 500 and 2452 m have sharp peaks at 6, 26 and 35 meV in the range of 0–50 meV. The spectrum of ice Ih also has a peak at 6 meV, which is assigned to the acoustic mode, and peaks at 26 and 35 meV, which are assigned to optic modes of translational lattice vibrations (LI and Ross, 1992). The energies and intensities of these peaks did not change with depth within the experimental resolution, but the shape of the spectra in the range of 16–21 meV is different at depths of 500 and 2452 m in depth, as is described below.

Figure 4A and B show the spectra of Vostok ice at depths of 500 and 2452 m in the range of 15–45 meV. The intensities of the spectra were normalized by the integrated

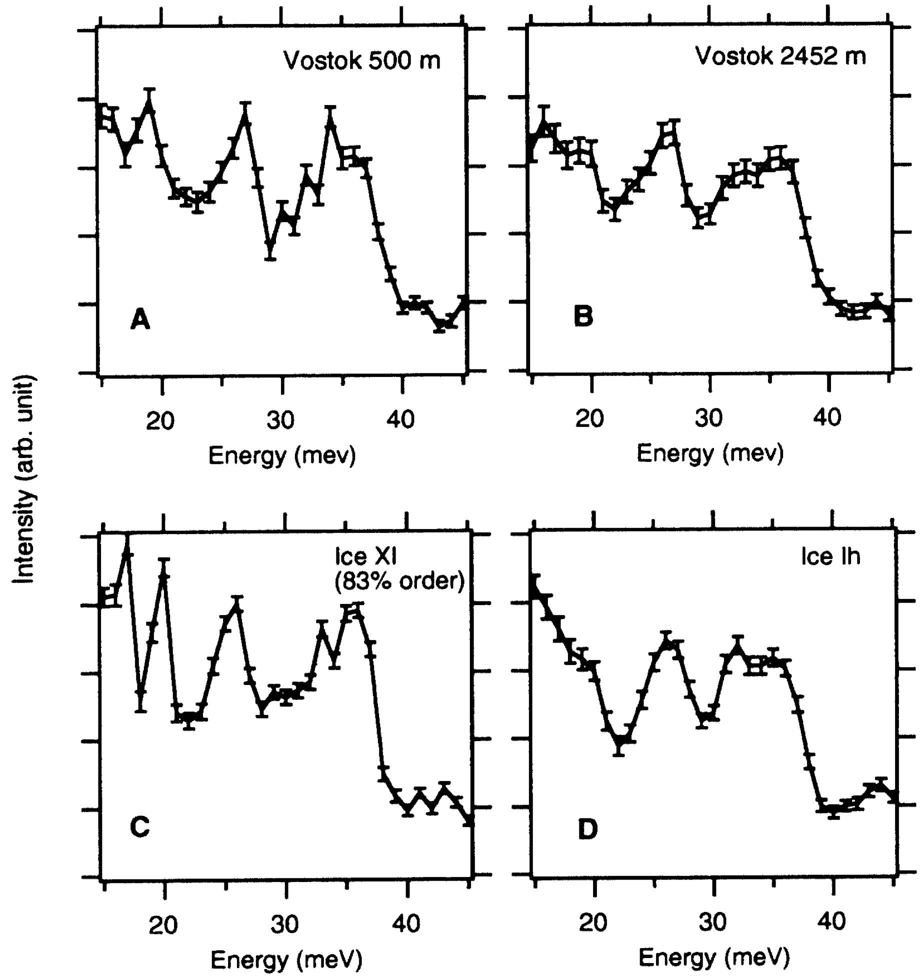

Fig. 4. IINS spectra from Vostok ice at depths of 500 m (A) and 2452 m (B) in the range of 15–45 meV. The spectra of (C) were obtained by ice XI with a proton-ordered structure and (D) by ice Ih with a proton-disordered structure (FUKAZAWA et al., 1998b). Measurements were made at 21 K. The intensities of the spectra were normalized by the integrated intensities of elastic scattering.

intensities of elastic scattering. The spectrum at 500 m in depth has a sharp peak at 19 meV that spreads from 17 to 21 meV. The intensity of the 19 meV peak is 8.0. The spectrum at 2452 m in depth has two weak peaks at 16 and 19 meV. These peaks are spread from 15 to 21 meV. The intensities of the 16 and 19 meV peaks are 7.2 and 6.4, respectively.

4. Discussion

As shown in Fig. 4A and B, there is a clear difference in the IINS in the region of 16–21 meV between Vostok ice at 500 and at 2452 m in depth. Since the IINS of ice Ih in the region of 16–21 meV is caused by translational lattice vibrations (LI and ROSS, 1992), the difference between Vostok ice at 500 and at 2452 m in depth is due to a change in the translational lattice vibrations. The change in the translational lattice vibrations is due to change in the arrangement of oxygen nuclei and protons. X-ray diffraction measurements have shown that the structure of oxygen nuclei has a hexagonal arrangement (space group $P6_3/mmc$) regardless of T_i (IKEDA, 1994). Thus, the difference between Vostok ice at 500 and at 2452 m in depth is considered to be caused by a change in the proton arrangement.

FUKAZAWA *et al.* (1998b) reported the IINS spectra of ice Ih and ice XI measured at 21 K using the CAT spectrometer. Figure 4C and D show the IINS spectra of ice XI and ice Ih. In ice XI at 21 K, 83% of the protons are ordered (FUKAZAWA *et al.*, 1998 b). Ice XI has two sharp peaks at 17 and 20 meV, which are caused by the B_1 vibrational mode in the proton-ordered structure (KLUG and WHALLEY, 1978), but such peaks are not observed in ice Ih. Furthermore, the peak intensity of the B1 mode (19 meV) of Vostok ice at 500 m in depth, which is clearly observed at 20 meV in the IINS spectrum of ice XI, is lower than that in Vostok ice at 2452 m in depth. The spectrum of Vostok ice at 2452 m in depth has two weak peaks at 16 and 19 meV, but these peaks are not caused by the B_1 mode because these peaks are broad and intensities are much lower. These results show that the translational lattice vibrations (16–21 meV) of Vostok ice at 500 m in depth are different from those of ice Ih and similar to those of ice XI. The translational lattice vibrations (16–21 meV) of Vostok ice at 2452 m in depth are similar to those of ice Ih. Thus, it is reasonable to consider that Vostok ice at 500 m in depth contains a proton-ordered arrangement and that Vostok ice at 2452 m in depth has a proton-disordered arrangement. This conclusion concerning Vostok ice is consistent with the theoretical ratios of ordered protons in ice (0.29 at $T_i=219$ K and 0 at $T_i=245$ K) that were calculated from the ratio of the intensity of the peak at 300 cm^{-1} to that at 220 cm^{-1} in translational lattice vibrations of DF ice based on Landau theory of second-order phase-transition (FUKAZAWA *et al.*, 1998a).

The measurements of the IINS of the Vostok ice indicate that a transition from a proton-disordered phase to a proton-ordered phase takes place in an Antarctic ice sheet, as was proposed by FUKAZAWA *et al.* (1998a). That is, the proton-ordered structure is thermodynamically stable when the ice temperature is lower than 237 K. FUKAZAWA *et al.* (1997) reported that the proton rearrangement in Vostok, Mizuho and Nansen ice, which is due to proton ordering, is not affected by ice sheet flow. Furthermore, they showed that proton ordering is not attained within the short term (for instance, 10 years). Thus, the change in the molecular orientation of ice is so slow that a thermodynamic equilibrium is not attained in a finite period of time (*e.g.*, less than 10 years) in the experimental studies. The artificial ice thus becomes frozen in a disordered state at temperatures lower than 237 K. Ice in an Antarctic ice sheet remains at nearly the same temperature for a very long period of time (*e.g.*, 10^4 years), and it remains in a thermodynamic equilibrium state.

Further analysis of the phase transition and the high transition temperature (237 K) is needed to understand the hydrogen bond in ice. In inland Antarctica, there is a large ferroelectric ordered ice mass from the surface to 2000 m in depth, as shown in Fig. 2B. Its thickness is more than half of the total ice thickness (about 3000 m).

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