Raman Spectra of Translational Lattice Vibrations in Polar Ice

Hiroshi Fukazawa,* Dai Suzuki, Tomoko Ikeda, and Sinji Mae

Department of Applied Physics, Hokkaido University, Sapporo 060, Japan

Takeo Hondoh

Institute of Low-Temperature Science, Hokkaido University, Sapporo 060, Japan

Received: October 11, 1996; In Final Form: February 3, 1997⊗

We measured the Raman spectra of Mizuho and Nansen ice recovered from Antarctica, and Dye-3 ice recovered from Greenland, to observe the translational lattice vibrations in polar ice. Since we investigated the effect of the aging on the ice and the ice temperature on the spectra, we chose to study the ice from three different sites. The ages of the ice Ih range from 4.6 to 100 kyr. The ice temperatures at the depth it was located range from 231 to 260 K. The results were compared with the measurements taken of the Vostok ice by Fukazawa et al. We found that the relative intensity of the peak at 300 cm^{-1} increased as the temperature at which the ice was kept for a long period increased from 214 to 237 K. Since this peak is assigned to a translational lattice vibration traveling along the hydrogen-bonding network, we conclude that the structure of the network in the polar ice varies with time at a very slow rate to attain an equilibrium state that has never been found on the laboratory time scale.

Introduction

The Raman spectra arising from translational lattice vibrations in ice Ih show two molecular-optic bands at 225 and 300 cm^{-1}.[1,2] The dynamical calculation given by Faure and Chosson[1,3] indicated that the peak at 300 cm^{-1} was due to LO (longitudinal-optic) vibrations corresponding to TO (transverse-optic) vibrations at 225 cm^{-1}. Klug and Whalley also indicated the TO−LO splitting using a more elaborate model.[4]

Inelastic neutron-scattering studies[5,6] revealed that there was a specific density of vibrational states for translational modes at 225 and 300 cm^{-1}. The model by Li and Ross,[7,8] in which strong and weak hydrogen bonds in the ratio of about 2:1 are randomly distributed in the structure of ice Ih, was shown to fit the experimental spectra with reasonable accuracy. They concluded that the peaks at 225 and 300 cm^{-1} of the spectra were caused by translational lattice vibrations traveling across the weak and strong hydrogen bonds, respectively.

If there are two kinds of the hydrogen bonds in ice Ih, a change in the peaks should be observed with a change of the hydrogen bonds. Thus, we measured the Raman spectra of Vostok ice recovered from Antarctica in order to observe the long-term aging effects on the hydrogen bonds of ice Ih.[9] We found that the ratio of the peak intensity at 300 cm^{-1} to 225 cm^{-1} ($I_{300/225}$) increased as the depth of the ice core increased from 500 to 2452 m. Since no change in the peak intensity was observed by pressurization,[10] the increase of $I_{300/225}$ can be attributed to the aging effect on the structural change of ice during the very long period from 28 to 209 kyr. According to the model by Li and Ross,[7,8] the increase of $I_{300/225}$ shows that the ratio of the number of the strong bonds to the weak bonds increases with age. The increase of the ratio implies that the proton arrangement in the Antarctic ice varies with a very long-term age.

But the reason for the change in the proton arrangement is not clear in this study because the ice temperature (T_i) at the depth it was located in the polar ice sheet changes with the depth and age. To determine the reason, we must investigate the effect of the aging on the ice (t) and the ice temperature (T_i), in relation to the spectra.

In the present study, we measured the Raman spectra of Mizuho ice and Nansen ice recovered from Antarctica and Dye-3 ice recovered from Greenland. The values of t and T_i ranged from 4.6 to 100 kyr and 231 to 260 K, respectively. The results show that the spectra are independent of t. The spectra were compared with those of Vostok ice measured by Fukazawa et al.,[9] and we found that $I_{300/225}$ increased as T_i increased from 214 to 237 K. The results show that the proton arrangement in the polar ice which had been stored below 237 K varies with the ice temperature.

Description of Ice Samples

Polar Ice. To obtain the present measurements, we used natural ice cores which was collected from two sites in Antarctica and one site in Greenland (Figure 1): Mizuho ice core (70°41′ S, 50°36′ E), Nansen ice (72°44′ S, 24°10′ E) in Antarctica, and Dye-3 ice core (65°12′ N, 43°47′ W) in Greenland.

The Mizuho ice cores were collected at depths of 410, 510, and 690 m by using a thermal drill in 1983 and 1984 by the Japanese Antarctic Research Expedition (JARE) at Mizuho station, Antarctica, where the annual mean air temperature is −32.4 °C. The ice cores were transported from the station to Japan, maintaining their temperature below −20 °C, and were stored in the cold room at −20 °C. No signs of partial melting or recrystallization were observed in the cores. The values of T_i and t at each depth are shown in Table 1.

The Nansen ice was collected at the Nansen ice field upstream of the Sør Rondane Mountains, Antarctica, by the Japanese Antarctic Research Expedition (JARE) in 1988 and 1989. The annual mean temperature at the site is approximately −42 °C, using the 10 m snow temperature method.[16] We estimate the Nansen ice to be older than 40 kyr but less than 100 kyr.[17]

The Dye-3 ice cores were recovered at Dye-3, South Greenland, in 1980 and 1981 by the international team of the

⊗ Abstract published in *Advance ACS Abstracts,* June 15, 1997.

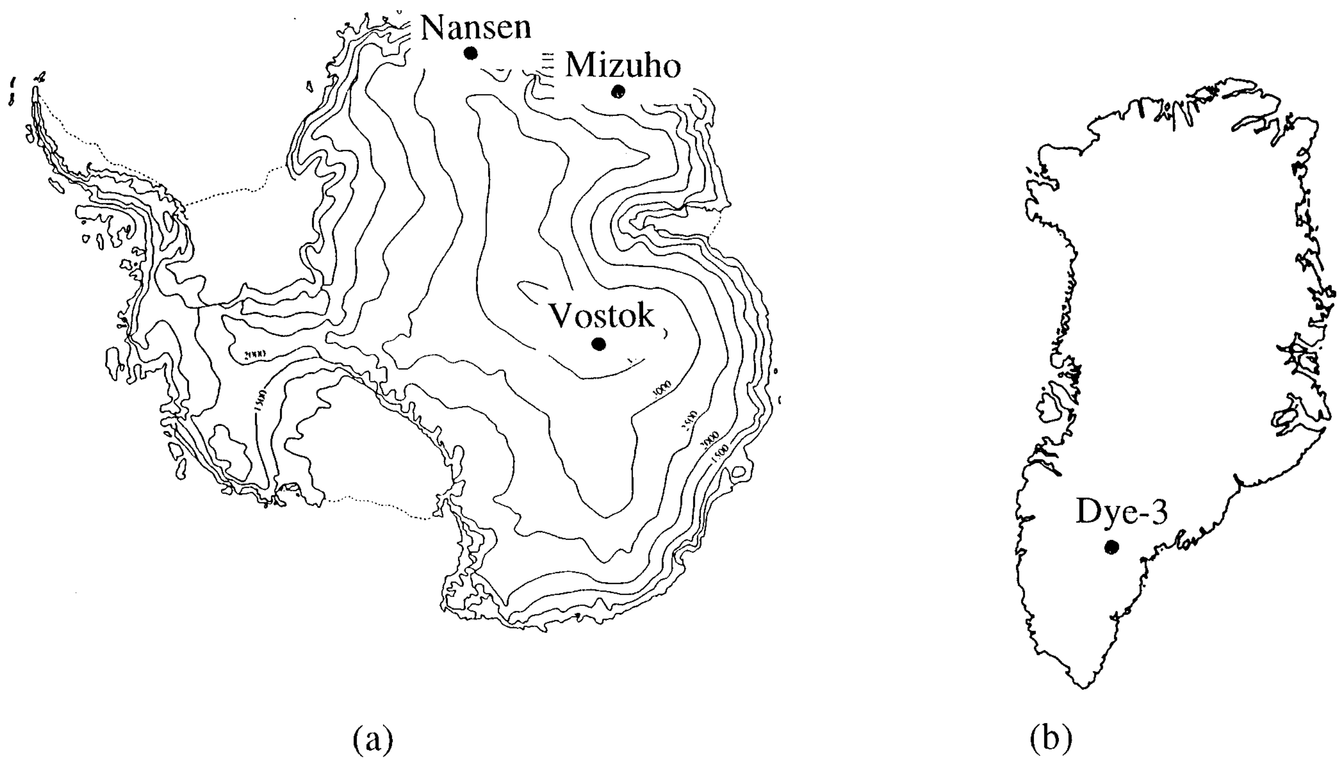

Figure 1. Drilling site of Mizuho, Nansen, and Dye-3 ice: (a) Antarctica, (b) Greenland.

TABLE 1: Temperature and Estimated Age of Polar Ice Measured in the Present Study

ice core	depth (m)	age t (kyr BP)	10 m temp T_{10} (K)	ice temp T_i (K)
Mizuho (ref 11)	410	4.6	237	237
	510	6.1	232	238
	690	7.8	235	238
Nansen	0.5	40−100		231
Dye-3 (ref 19)	1501	5.8	252	255
	1687	8.3	252	257
	2000	100	247	260

Greenland Ice Sheet Program. The annual mean air temperature is −19.6 °C at the station. The cores were stored in the cold room at −40 °C. The values of T_i and t at each depth are shown in Table 1. As the table shows, T_i increases greatly as the depth does.

Artificial Ice. To examine the aging effect on artificial ice, ice made by the modified Bridgman method[23] was cut into layers and examined. It was then compared to old ice which had been stored at 253 K for 18 yr in a cold room.

Method of Measurements

A series of Raman spectra were measured by the JOBIN YVON RAMANOR T64000, which was calibrated to 0.1 cm^{-1} by recording the standard emission lines of the neon emission lines. This instrument, which is equipped with a CCD detector, allows simultaneous recording of the frequency range between 50 and 400 cm^{-1}, including the translational lattice vibration modes. The excitation energy for Raman emission was produced by Ar ion laser using monochromatic radiation of 514.5 nm with an output of 300 mW. The spectral resolution was 0.45 cm^{-1} for all spectra.

Rectangular specimens of the ice (size 3 × 3 × 2 mm) were cut from the natural and artificial ice. The natural samples included many crystal grains with diameters of 0.5−7.0 mm. An incident laser beam was focused on a crystal grain with a diameter of 1 μm under an optical microscope which was connected to the spectrometer for 180° scattering measurements. We measured the spectra at three different locations within a crystal grain of Mizuho ice (690 m depth), and the spectra did not change with the location. No effect induced from air bubbles was observed.

It was revealed that the Raman intensity at 225 and 300 cm^{-1} varied with the orientation of the *c*-axis.[3,9,24] The value of $I_{300/230}$ for $\theta = 0°$ is about 3% higher than that of $\theta = 90°$.[9] θ is the angle that the polarization plane of the incident laser beam makes with the orientation of *c*-axis of the ice. We observed four spectra at the measurements of $\theta = 0°$, 30°, 60°, and 90° for each sample. The orientation of the *c*-axis in each crystal grain was determined using the Rigsby stage.

The samples of ice were mounted on the cold tip of a UV202CL helium-cooled refrigerator, and the temperature of the samples was kept at 185 ± 1.5 K during the measurements.

Results

$I_{300/225}$ of Polar Ice. We measured the Raman spectra to observe the peak intensity at 225 and 300 cm^{-1} in the polar ice. All spectra have two main peaks at 225 and 300 cm^{-1}. Figure 2 shows the spectra for Mizuho ice (410 m depth), Nansen ice (0.5 m depth), and Dye-3 ice (1501 m depth) when θ is 0°. The intensities are normalized by the peak intensity of 225 cm^{-1}. The peak frequencies in polar ice are identical with those of artificial ice Ih.[1,2]

The values of $I_{300/225}$ for Mizuho, Dye-3, and Nansen ice in Figure 2 are 0.37, 0.38, and 0.38, respectively. The values are similar to that of artificial ice Ih. No significant change in the spectra among these three kinds of polar ice was obtained.

Figure 3a shows the depth profile of $I_{300/225}$ of the three kinds of polar ice. We used the band areas for the intensities at 300 and 225 cm^{-1}. The values of $I_{300/225}$ in Figure 3a are the average of the measurements at $\theta = 0°$, 30°, 60°, and 90°. The intensities are almost similar to that of artificial ice Ih, but the

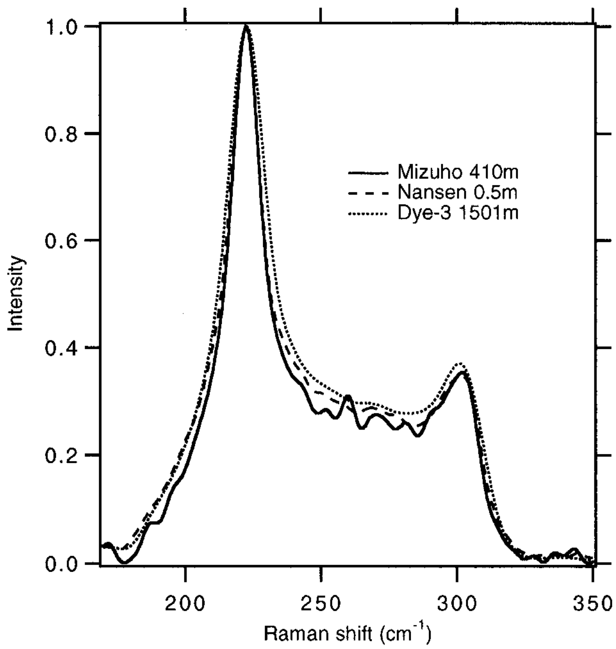

Figure 2. Raman spectra of polar ice. The solid, broken, and dotted line are the spectra of Mizuho, Nansen, and Dye-3 ice, respectively.

value of Mizuho ice at 510 m depth is 0.01 smaller than that of Mizuho ice at 410, and 690 m depth.

Aging Effect on Artificial Ice. To examine the aging effect in a cold room, we measured the Raman spectra of two kinds of artificial ice: one was stored for 1.5 yr, and the other was stored for 18 yr at 253 K. There was no difference between the spectra, and no aging effect was observed.

Discussion

Effect of Depth, Age (t), and Temperature (T_i) on $I_{300/225}$. As shown in Figure 3a, the depth of Mizuho, Nansen, and Dye-3 ice varies from 0.5 to 2000 m. Figure 3b shows the age (t) dependence of $I_{300/225}$, and $I_{300/225}$ is constant regardless of t. The value of $I_{300/225}$ is approximately the same value of 0.289. Figure 3c shows the temperature (T_i) dependence of $I_{300/225}$. The value of $I_{300/225}$ is plotted against $1/T_i$. The solid line in Figure 3c is the regression line in the range 237−260 K. The results show that there is negligible change of $I_{300/225}$ of polar ice in the range 237−260 K. Thus,

$$\text{if } T_i \geq 237,\ I_{300/225} = 0.289 \pm 0.011 \tag{1}$$

The $I_{300/225}$ of the Vostok ice[9] are shown as open circles in Figure 3a−c. $I_{300/225}$ of Vostok ice at 500 m in depth is 4% smaller than that of artificial ice Ih. Figure 3a shows that depth (d km) has a clear effect on $I_{300/225}$ for Vostok ice ($I_{300/225-V}$). The value calculated by linear regression is given by

$$I_{300/225-V} = 0.231 + 0.029d \tag{2}$$

Figure 3b shows that t kyr has an effect on $I_{300/225-V}$. The value calculated by linear regression is given by

$$I_{300/225-V} = 0.231 + 0.00034t \tag{3}$$

On the other hand, the value of $I_{300/225}$ increases with T_i in the range 214−237 K as shown in Figure 3c. The solid line in the figure is the regression line, and the value of $I_{300/225}$ is given by

$$\text{if } T_i \leq 237\text{ K},\quad I_{300/225} = 274.73 \exp(-E/kT_i) - 273.91 \tag{4}$$

where k is gas constant, and E was calculated to be 0.79 kcal/mol.

Equation 4 shows that $I_{300/225}$ in the polar ice which had been stored below 237 K increase with T_i . Since the peaks at 225 and 300 cm^{-1} are assigned to a translational lattice vibration traveling along the hydrogen bonds,[1−4,6−8] we conclude that the structure of the hydrogen bonds in the polar ice varies with T_i . According to the model by Li and Ross,[7,8] the increase of $I_{300/225}$ shows the increase of the ratio of the strong bonds/weak bonds. Since the increase of the ratio is caused by the proton rearrangement in ice Ih, we conclude that the proton configurations in ice Ih varies with the temperature of the ice.

Increasing $I_{300/225}$ with T_i. We found that $I_{300/225}$ of polar ice increase with T_i in the range 214−237 K. This phenomena may be caused by a change in the hydrogen-bonding network. If we assume that ice Ih is constructed by the two kinds of hydrogen bonds which show peaks at 225 and 300 cm^{-1} in the Raman spectrum, the increase in $I_{300/225}$ with T_i shows that the bond at 225 cm^{-1} is different from the bond at 300 cm^{-1} in the internal energy as follows.

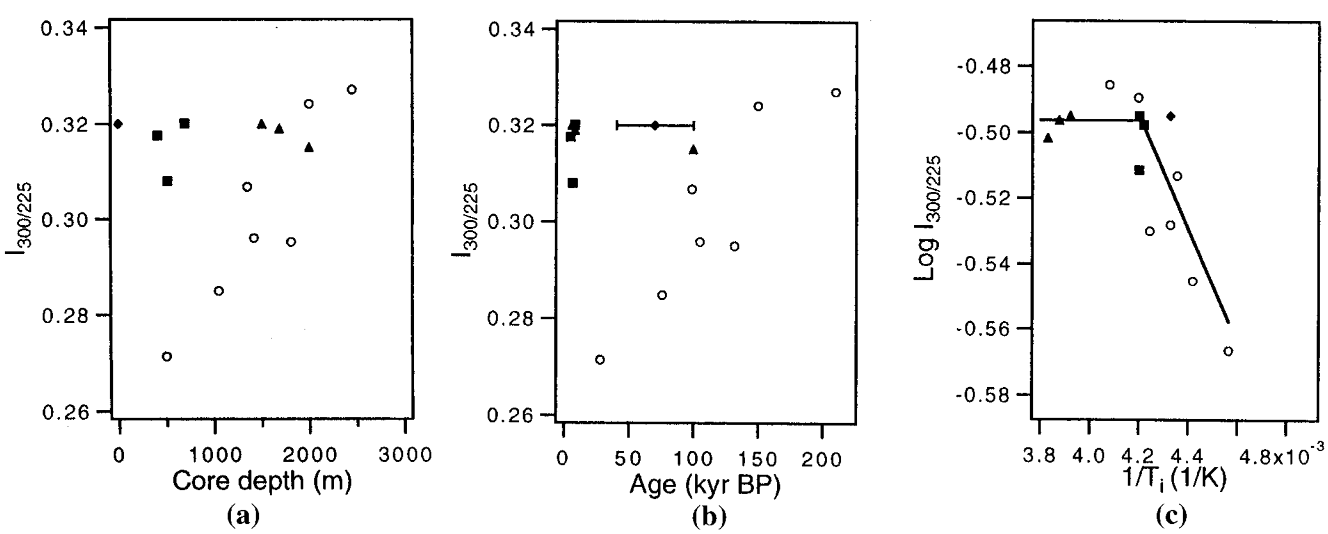

Figure 3. (a) Depth dependence of $I_{300/225}$. (b) Age (t) dependence of $I_{300/225}$. (c) Temperature (T_i) dependence of $I_{300/225}$. The circles, squares, diamonds, and triangles are the data for Vostok, Mizuho, Nansen, and Dye-3 ice, respectively. The solid lines in (a) and (b) represent eq 2 and eq 3, respectively. The solid line in (c) was computed using a least-squares program.

When the two bonds (the internal energy, E_{225} and E_{300}) are under equilibrium conditions, the free energy is written as the sum of the two components[25]

$$F = X_{225}E_{230} + X_{300}E_{300} + kT_i(X_{225} \ln X_{225} + X_{300} \ln X_{300}) \quad (5)$$

where X_{230} and X_{300} are mole fractions of the two bonds k is the gas constant. From eq 5, the fraction of the two bonds is given by

$$X_{225}/X_{300} = \exp(-\Delta E/kT_i) \quad (6)$$

where ΔE is $E_{300} - E_{225}$. Equation 6 shows that X_{300}/X_{225} changes with T_i. If E_{300} is larger than E_{225}, X_{300}/X_{225} increases with T_i. Thus, the increase of $I_{300/225}$ as shown in eq 4 suggests that E_{300} is larger than E_{225}. When T_i is over 237 K, the value of $I_{300/225}$ is constant as shown in eq 1. This phenomenon shows that E_{300} is equal to E_{225} when T_i is over 237 K.

Aging Effect on Spectra of Translational Lattice Vibration. As shown in Figure 3c, the value of $I_{300/225}$ seems to be a monotonic function of temperature. However, no significant temperature dependence was observed when the temperature of an artificial ice was increased from 10 to 263 K at a rate of 3 K/h.[26] Temperature of polar ice changes at a very slow rate during the ice sheet flow. Therefore, it is plausible that the temperature dependence shown in Figure 3c was brought by a long-term aging effect on the spectra. Since a rate of the temperature change is of the order of 0.1 K/yr for the largest case in Mizuho ice, this aging effect has a relaxation of about 10 yr/K.

Summary

We measured the Raman spectra of natural ice Ih recovered from Antarctica and Greenland. We found that the relative peak intensity at 300 cm^{-1} increased as the temperature at which the ice was kept for a long period increased from 214 to 237 K. For Vostok ice, the intensity increased with both depth and age. Since this peak is assigned to the translational lattice vibration traveling along the hydrogen bond, the results show that proton arrangement in the polar ice varies with depth, age, and temperature.

References and Notes

(1) Faure, P.; Kahane, A. *Phonons*; Nusimovici, M. A., Ed.; Flammarion Science: Paris, 1971; p 243.

(2) Wong, P. T. T.; Whalley, E. *J. Chem. Phys.* **1976**, *64*, 2359.

(3) Faure, P.; Chosson, A. *J. Glaciol.* **1978**, *21*, 65.

(4) Klug, D. D.; Whalley, E. *J. Glaciol.* **1978**, *21*, 55.

(5) Klug, D. D.; Whalley, E.; Svensson, C.; Root, J. H.; Sears, V. F. *Phys. Rev.* **1991**, *B44*, 844.

(6) Li, J. C.; Ross, D. K. In *Proceedings of the International Conference on Physics and Chemistry of Ice*; Maeno, N., Hondoh, T., Eds.; Hokkaido University Press: Sapporo, 1992; p 27.

(7) Li, J. C.; Ross, D. K. *Nature* **1993**, *365*, 327.

(8) Li, J. C.; Bennington, A. M.; Ross, D. K. *Phys. Lett.* **1994**, *A192*, 295.

(9) Fukazawa, H.; Ikeda, T.; Hondoh, T.; Lipenkov, V. Ya.; Mae, S. *Physica B* **1996**, *219&220*, 466.

(10) Johari, G. P.; Sivakumar, T. C. T. *J. Chem. Phys.* **1978**, *69*, 12.

(11) The ice temperature in the bore hole was measured by a thermister probe.[12] Using the relation between oxygen-isotope ratio[13] and mean annual temperature for ice cores at 10 m snow temperature[14] in Mizuho plateau, we estimated the temperature for the ice which was at the surface of the ice sheet. Ice age of the Mizuho cores was dated by Nakawo et al. using the vertical strain rate derived from fabric data of the cores.[15]

(12) Okudaira, F.; Nishio, F.; Ikegami, K. *Nankyoku Shiryou* **1988**, *32*, 277.

(13) Higashi, A.; Nakawo, M.; Narita, H.; Fujii, Y.; Nishio, F.; Watanabe, O. *Ann. Glaciol.* **1988**, *10*, 52.

(14) Watanabe, O.; Fujii, Y.; Satoh, K. *Ann. Glaciol.* **1988**, *10*, 188.

(15) Nakawo, M.; Ohmae, H.; Nishio, F.; Kameda, T. *Proc. NIPR Symp. Meteorol. Glaciol.* **1989**, *2*, 105.

(16) Satow, K. *Mem. Natl. Inst. Polar Res., Spec. Issue (Jpn.)* **1978**, *7*, 63.

(17) Since South Yamato ice core, which is estimated to be 40 kyr,[18] is considered to be younger than the Nansen ice, the age of the Nansen ice is older than 40 kyr. From the ice flow at the upstream, we estimate that the age of Nansen ice is younger than 100 kyr.

(18) Machida, T. Thesis of Touhoku University, 1992.

(19) Temperature measured in the bore-hole.[20] Using the relation between oxygen-isotope ratio and mean annual temperature for ice cores at 10 m snow temperature,[21] we estimated the temperature for the ice which was at the surface of the ice sheet. The age of the cores was estimated by Dansgaard et al.[22]

(20) Gundestrup, N. S.; Hansen, B. L. *J. Glaciol.* **1984**, *30*, 282.

(21) Johnsen, S. J.; Dansgaard, W.; White, J.W. C. *Tellus* **1989**, *41B*, 452.

(22) Dansgaard, W.; Clausen, H. B.; Dahl-Jensen, D.; Gundestrup, N.; Hammer, C. U. In *Current Issues in Climatic Research, Proceedings of the European Economic Community Climatology Programme*; Ghazi, A., Fantechi, R., Eds.; Symposium, Sophia Antipolis: France, 1984; p 45.

(23) Oguro, M.; Higashi, A. *Philos. Mag.* **1971**, *24*, 713.

(24) Scherer, J. R.; Snyder, R. G. *J. Chem. Phys.* **1977**, *67*, 4794.

(25) Swalin, R. A. *Thermodynamics of Solids*, John Wiley and Sons: New York, 1962.

(26) Fukazawa, H. Thesis of Hokkaido University, 1994.