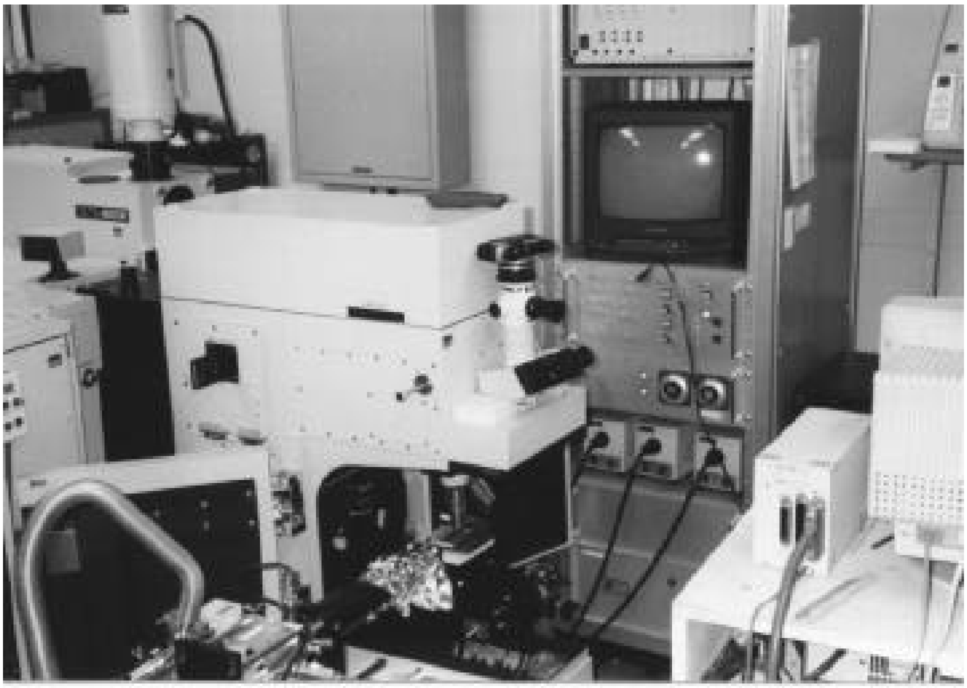
6. Observation of the vicinity of ice lens by Raman spectroscopy (Exp. 4)

Knowledge of the ice configuration in the vicinity of a growing ice lens is important for clarifying the mechanism of the formation of ice lenses. In this chapter, the ice configuration in the vicinity of the warmest ice lens in the freezing porous medium was investigated by combining Raman spectroscopy with the unidirectional freezing experiments. Such experiment, which can investigate the ice configuration on the scale of micrometer, has not carried out yet.

6.1 Sample and method

The sample used here was the sample 2 (d = 9.7 μm). Water-saturated porous medium was prepared by placing the glass particles in a desiccator with water, evacuating the desiccator, allowing a few days for the solid-vapor equilibrium to be established, adding liquid water, and allowing the system to equilibrate for one day. Initial water content of the sample was 80 %. The prepared sample was placed into a sample cell shown in figure 14 and set in the unidirectional freezing apparatus equipped with Raman spectrometer. Before the unidirectional freezing experiment, the cell was initially cooled to 2 ˚C. The sample was frozen using the unidirectional freezing apparatus with the temperature gradient of 0.33 ˚C/mm, and water in the vicinity of a growing ice lens was observed by the Raman spectroscopy. In this experiment, we did not control the freezing rate same as the **Exp. 1**. The temperature of growth surface of ice lens was estimated by temperatures measured by two copper-constantan thermocouples inserted into the sample cell.



Photograph 5. Raman spectroscopy.

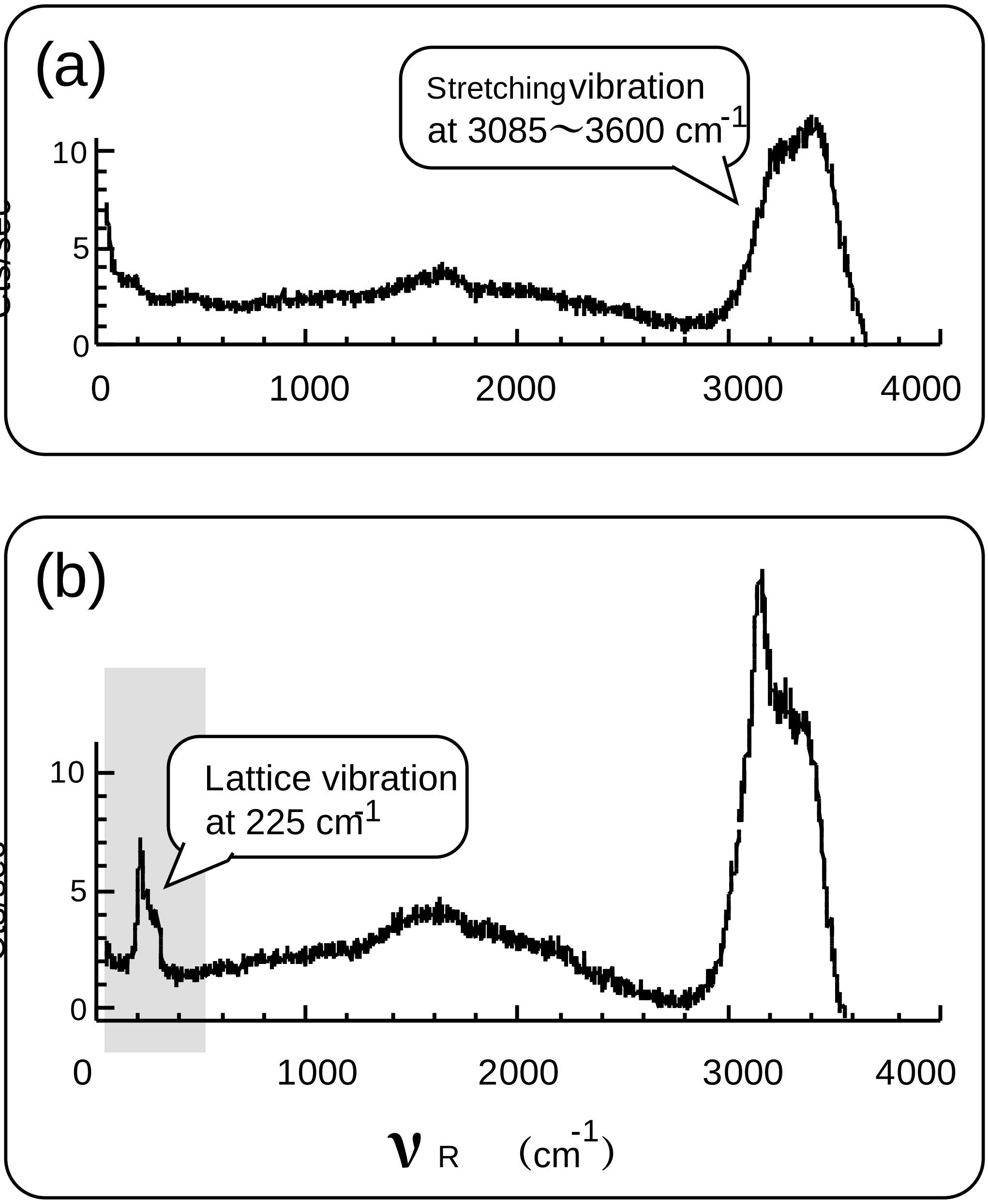


Fig. 29. The Raman spectra obtained from samples at room temperature (a) and the temperature of liquid nitrogen (b). The Raman spectrum arising from translational lattice vibrations in ice Ih shows a molecular-optic band peak at 225 cm^{-1}.

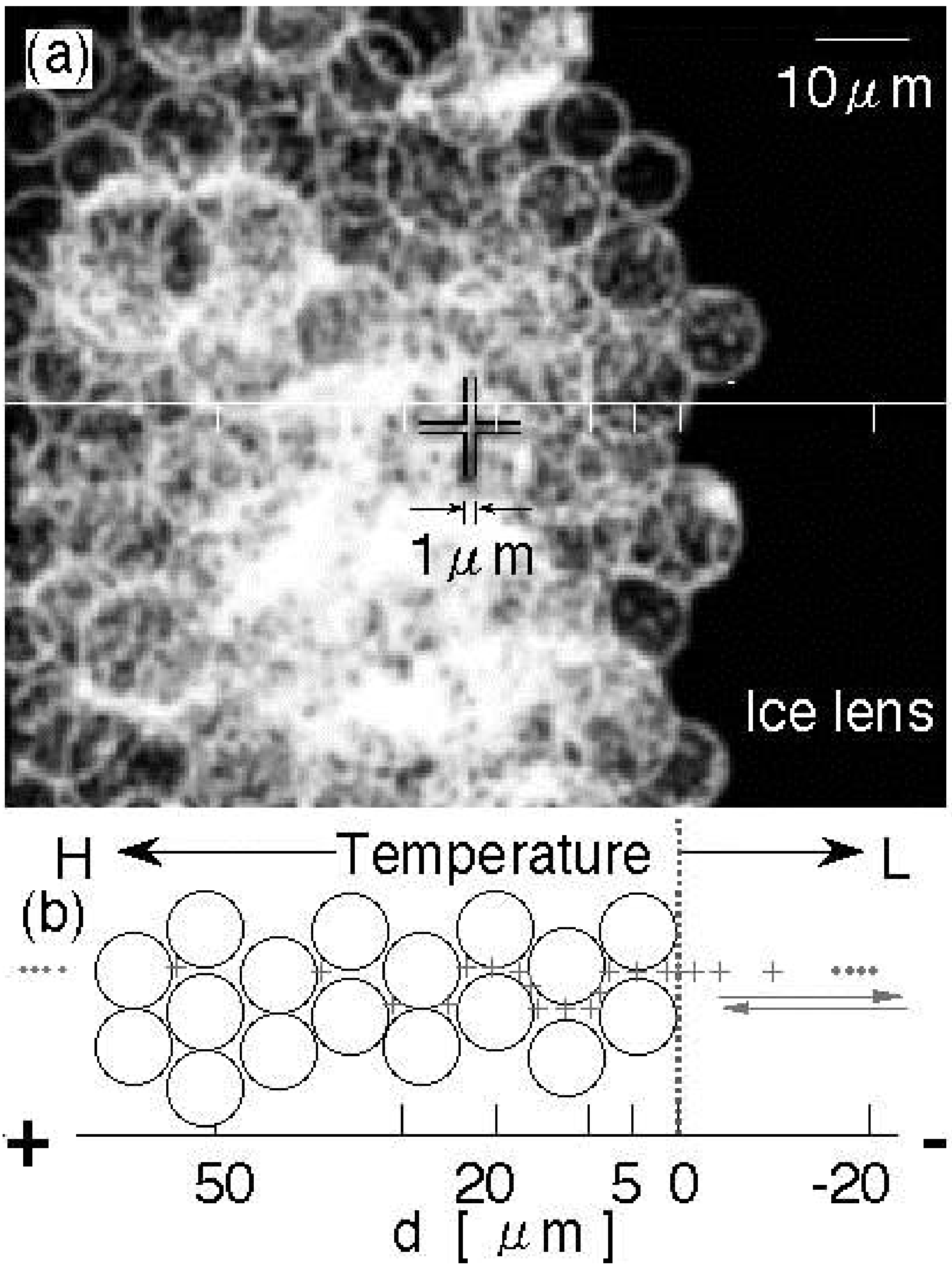


Fig. 30. A computer-processed image of the vicinity of the growth surface of the ice lens monitored using the Raman system. The right side is colder and the left side is warmer. The warmest ice lens appears black, and the glass particles appear as white circles. The diagnostic spot was moved in 0.4-micrometer steps as shown in (b), where d is the distance from the growth surface of the warmest ice lens.

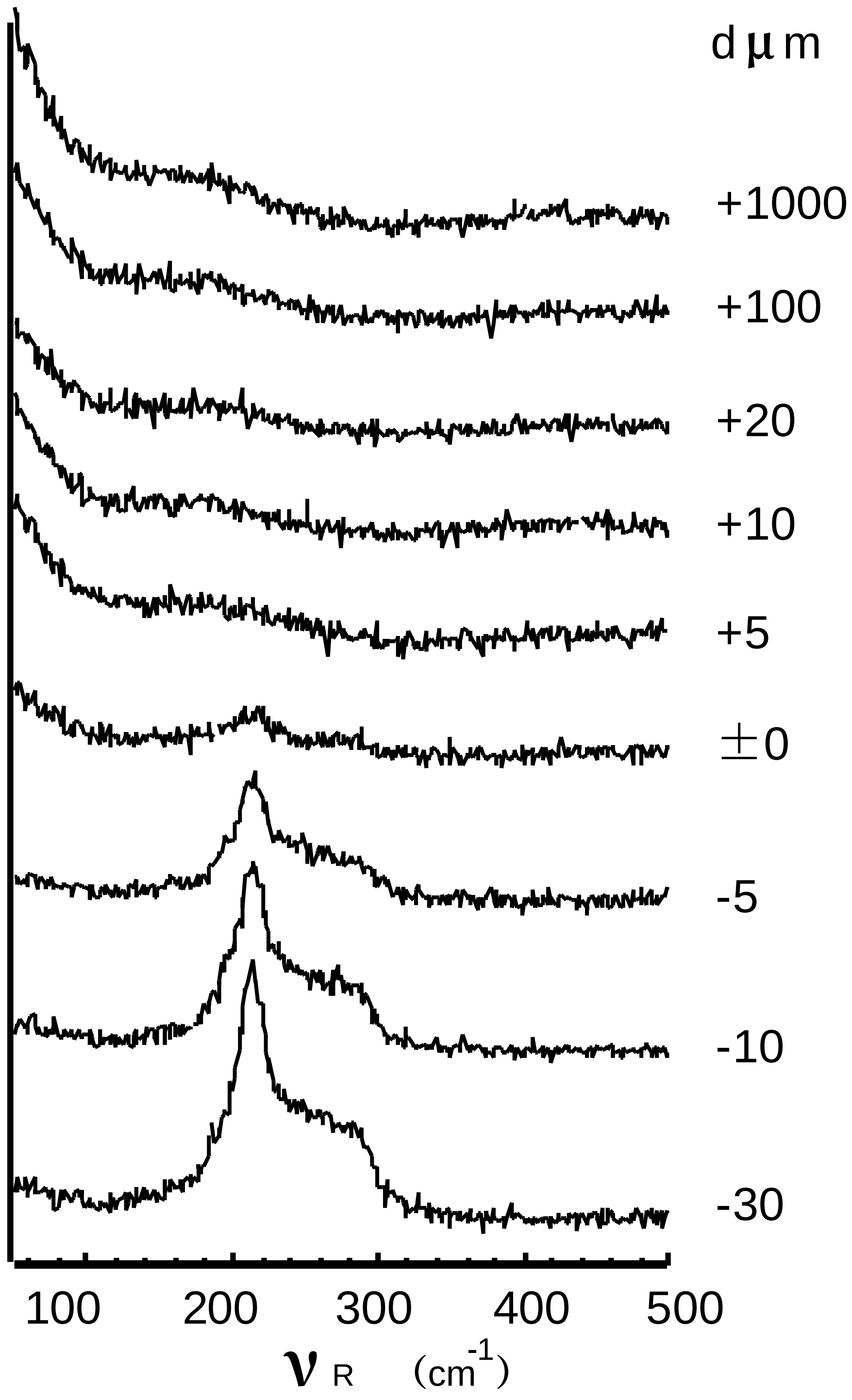


Fig. 31. A series of the Raman spectra obtained from pores at distance d.

6.2 Raman spectroscopy

The Raman spectrum arising from translational lattice vibrations in ice Ih shows a molecular-optic band peak at 225 cm^{-1} (Wong and Whalley, 1975; Fukazawa et al., 1997). If ice exists, this peak should be observed. While the warmest ice lens was growing, water in the vicinity of the growth surface was investigated using a Raman spectroscope (JOBIN YVON RAMANOR T64000: photograph 5), which was placed above the sample cell. The Raman spectroscope was calibrated to 0.1 cm^{-1} by recording the standard emission lines of Neon. This instrument was equipped with a charge coupled device detector that allows simultaneous recording of the frequency range between 50 and 400 cm^{-1}. The excitation energy for Raman emission was produced by an Argon ion laser using monochromatic radiation of 514.5 nm with an output of 150 mW. The spectral resolution was 0.45 cm^{-1} for all spectra. The incident laser beam was focused on a spot of the freezing sample 1 μm in diameter, under a microscope. The time elapsed during each measurement was 30 sec. Since the ice lenses that we observed grew less than 0.5 μm during each measurement, we neglected the growth of the ice lens during the measurement period.

6.3 Experimental results

In order to evaluate the influence of the sample cell and glass particles on the Raman spectra, preliminary experiments were carried out using samples at room temperature and the temperature of liquid nitrogen. No remarkable peaks arising from the sample cell and the glass particles were observed in the frequency range between 50 and 400 cm^{-1} from either sample (figure 29).

When different temperatures were applied to either end of the sample cell, ice lenses formed similar to the ice lenses shown in figure 15. The temperature gradient near the warmest ice lens shown in the sample was 0.25 ˚C/mm and the temperature at the growth surface of the ice lens was estimated to be -0.06 ˚C. Then, we measured the Raman spectra to observe the peak at 225 cm^{-1} in the vicinity of the warmest ice lens that had grown for 300 minutes. Figure 30a shows a computer-processed image of the vicinity of the growth surface of the ice lens monitored using the Raman system. The right side is colder and the left side is warmer. The warmest ice lens appears black, and the glass particles appear as white circles. To measure each pore, the diagnostic spot was moved in 0.4-micrometer steps, as shown in figure 30b, where d is the distance from the growth surface of the warmest ice lens.

Figure 31 shows a series of the Raman spectra obtained from pores at distance d. The spectrum in the ice lens ($d < 0$) had a strong peak at 225 cm^{-1}, which indicated the existence of ice Ih. The peak was also observed in the spectrum at the boundary between a glass particle and the ice lens ($d = 0$). On the other hand, the spectrum at a warmer pore more than 5 μm away from the ice lens ($d > 5$) had no remarkable peak at 225 cm^{-1}, and was very similar to that of the sample at room temperature (figure 29a).

6.4 Discussion

If enough water reaches the growth surface of an ice lens, the ice lens will keep growing. If there is not enough water, however, the ice lens will stop growing and another ice lens will start to form in a new location. Therefore, water near the growth surface is important for ice lens formation. In our experiment, no ice larger than 1 μm was observed in pores at locations warmer than the growing ice lens. In nucleation, only aggregates larger than a critical size are stable and grow to become the solid phase. The size of the aggregates depends on the temperature and decreases with the temperature. Assuming a cylindrical solid in liquid at a temperature of T, the critical radius r_* is given by the Gibbs-Thomson effect:

$$r_* = \frac{\gamma}{\rho_s q}\frac{T_m}{T_m - T} \quad , \tag{29}$$

where γ is the solid-liquid interfacial free energy, ρ_s is solid density, q is the latent heat of melting, and T_m is bulk melting temperature. With $\gamma = 29 \times 10^{-3}$ J/m, $\rho_s = 0.917 \times 10^3$ kg/m^3 and $q = 3.33 \times 10^5$ J/kg (Ishizaki *et al*. 1996), we obtain $r_* = 0.026 / (T_m - T)$, where r_* is measured in µm. Consequently, the calculated critical diameter at the pores warmer than the growth surface of the warmest ice lens, which had an estimated temperature was -0.06 ˚C, is more than 0.87 µm. In addition, ice formation is more difficult in a pore than in bulk water because of surface forces from surrounding particles (Handa *et al*., 1992; Ishizaki *et al*., 1996). The estimated diameter only gives the smallest value and suggests that no ice smaller than about 1 µm exists in pores at positions warmer than the warmest growing ice lens. Therefore, no pore ice exists in any location warmer than the growth surface of the warmest ice lens in the porous medium consisted of glass particles with diameter of 9.7 µm and the ice lens grows without penetrating the warmer pores.

6.5 Summary

Unidirectional freezing experiments were carried out on an unconfined, water-saturated, uniform, porous medium consisting of micro glass particles with diameter of 9.7 µm. The formation of ice lenses was observed in the porous medium as same as shown in the **Exp. 1**. The Raman spectrum of water was used to clarify the ice configuration in the vicinity of the growing ice lens. No ice was found in any pore warmer than the warmest ice lens in the porous medium and the ice lens grew without penetrating the warmer pores. This result indicates that the growth surface of active ice lens correspond to the freezing front in the porous media.