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Inelastic Neutron Scattering of Amorphous Ice

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We measured the inelastic neutron scattering from high-density amorphous (HDA) and low-density amorphous (LDA) ice produced by pressurizing and releasing the pressure. We found a clear difference between the intermolecular vibrations in HDA and those in LDA ice: LDA ice has peaks at 22 and 33 meV, which are also seen in the spectrum of lattice vibrations in ice crystal, but the spectrum of HDA ice does not have these peaks. The excitation energy of librational vibrations in HDA ice is 10 meV lower than that in LDA ice. These results imply that HDA ice includes 2- and 5-coordinated hydrogen bonds that are created by breakage of hydrogen bonds and migration of water molecules into the interstitial site, while LDA ice contains mainly 4-coordinated hydrogen bonds and large cavities. Furthermore, we report the dynamical structure factor in the amorphous ice and show that LDA ice is more closely related to the ice crystal structure than to HDA ice.

KEYWORDS: ice, hydrogen bond, amorphous, neutron scattering, dynamics

§1. Introduction

In the hypothesis of liquid-liquid phase transition for the anomalies of supercooled water,1) liquid exists in two phases of different densities: high-density liquid (HDL) and low-density liquid (LDL). Mishima and Stanley2) investigated the decompression-induced melting of ice and reported that the volumes of HDL and LDL are continuous with the volumes of the high-density amorphous (HDA) and low-density amorphous (LDA) phases of ice. Therefore, knowledge of the physical properties in HDA and LDA phases, such as the structure and vibrational dynamics, would lead to an understanding of the anomalies of water.

HDA ice (about 1.1 g/cm^3) is produced by slow vapor-deposition at a temperature less than 30 K3,4) or pressurizing ordinary ice (ice Ih) to 1 GPa at 77 K.5,6) HDA ice that is produced by pressurizing is transformed to LDA ice (about 0.9 g/cm^3) by releasing the pressure at 77 K and warming to 130 K.5,6) LDA ice can also be produced by vapor deposition7) or by hyperquenching of water droplet.8)

Floriano *et al.*9) measured neutron diffraction of HDA ice and compared the pair distribution functions between HDA ice and liquid water at about 1 GPa and 312 K. The functions were found to be very similar, indicating that the structure of the first and second-neighbor molecules in HDA ice is very similar to that in liquid water. Klug *et al.*10,11) and Li and Jenniskens12) measured the incoherent inelastic neutron scattering (IINS) spectra of HDA and LDA ice produced by pressurizing and warming, and they reported a difference in peak energy in librational vibrations (40-120 meV) between HDA and LDA ice. Kolesnikov *et al.*13) measured the IINS spectrum of LDA ice produced by vapor deposition, and they observed two peaks in intermolecular vibrations (15-40 meV).

We measured the inelastic neutron scattering spectra of HDA, LDA and crystal ice (ice Ic) in order to investigate the dynamics of the amorphous ice. We compared the spectra obtained from HDA, LDA ice and ice Ic, and investigated the difference between intermolecular vibrations in HDA and LDA ice. We also examined the dynamical structure factor, *S(Q, E)*, which is directly related to the existence of vibrations with momentum hQ and energy E transfer, in the amorphous ice samples.

§2. Experimental

Samples of HDA ice (H_2O and D_2O) were made by compressing ice Ih in a piston cylinder apparatus to 1.2 GPa at 77 K. Each sample was recovered at zero pressure and 77 K, packed in an aluminum holder at 77 K, mounted on a cold refrigerator, and cooled to 21 K for measurements. The structure of HDA ice does not change when the pressure is reduced to ambient values if the sample has been kept at 77 K, because the orientation of water molecules at 77 K does not change. LDA ice and ice Ic were made by annealing at 130 and 160 K successively. Each LDA ice and ice Ic sample was cooled to 21 K for measurements. Inelastic neutron scattering measurements were performed at the pulsed neutron source KEK, Japan. The IINS spectra of H_2O ice and *S(Q, E)* of D_2O ice were obtained using the CAT spectrometer and the INC spectrometer (incident energy, 103 meV), respectively.

§3. Results and Discussion

3.1 Intermolecular vibrations

Figure 1a, 1b and 1c shows the IINS spectra of HDA, LDA ice and ice Ic respectively in the energy range of 0-140 meV. The spectrum of HDA ice has a strong peak at 5 meV that is spread from 3 to 35 meV. The full width at half-maximum (FWHM) of the peak is 10 meV. The spectrum of LDA ice has a sharp peak at 6 meV that

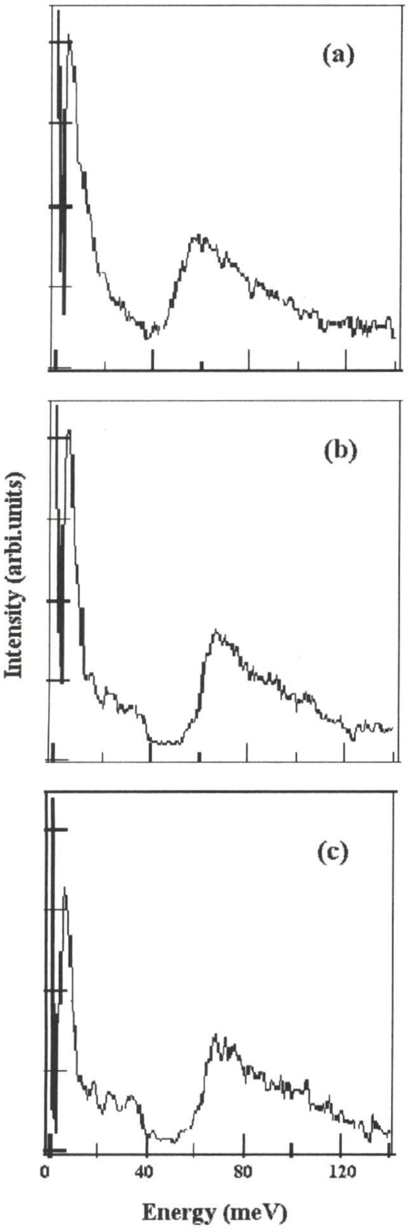

Fig. 1. Incoherent inelastic neutron scattering spectra of (a) high-density amorphous (HDA) ice, (b) low-density amorphous (LDA) ice, and (c) ice Ic.

is spread from 3 to 12 meV. The FWHM of the peak is 7 meV, which is smaller than that in HDA ice. The spectrum of ice Ic also has a sharp peak at 6 meV, which is assigned to the acoustic mode.[14] The FWHM of the peak is 5 meV, which is smaller than that in HDA and LDA ice.

The spectrum of HDA ice does not have a peak in the energy range of 15-40 meV. The spectra of crystal ice Ih [14,15] and Ic have two sharp peaks at 26 and 35 meV, which are assigned to translational lattice vibrations (i. e., intermolecular modes). Using molecular dynamics (MD) calculation, Tse[16] investigated the relationship between the calculated vibrational spectra of amorphous ice and the distribution of oxygen coordination numbers. Since he reported that these peaks at about 26 and 35 meV disappeared in the calculated spectrum of the amorphous ice including 2- and 5-coordinated hydrogen bonds, we think that our sample of pressure-induced HDA ice includes 2- and 5-coordinated hydrogen bonds. The 2- and 5-coordinated hydrogen bonds are created by breakage of hydrogen bonds and migration of water molecules into the interstitial site, and there is therefore a lack of large cavities in HDA ice.

The spectrum of LDA ice has a sharp peak at 22 meV and a broad peak at 33 meV. Ice Ic also has clear peaks at 26 and 35 meV. MD calculation[16] showed that the spectrum of amorphous ice made of mainly 3- and 4-coordinated hydrogen bonds has peaks at 26 and 35 meV. The percentages of 3- and 4-coordinated hydrogen bonds in this structure are about 7% and 93%, respectively. Thus, LDA ice contains 3- and 4-coordinated hydrogen bonds and has large cavities that are characteristic of crystal ice. Since the 35-meV peak in ice Ih is caused by the contribution of long-range dipole-dipole interaction to intermolecular vibrations,[17] a long-range order of 4-coordinated hydrogen bonds is thought to exist in LDA ice.

The vibrational spectrum of supercooled water is similar to that of LDA ice: the Raman spectra of supercooled water at about 260 K also have a peak at the 22-meV,[18,19] which is observed in the spectrum of LDA ice. However, the peak disappears in the vibrational spectra of liquid water at room temperature.[20] The broad features in the energy range of 15-40 meV both of HDA ice and liquid water at room temperature show the resemblance of HDA ice to normal liquid-water. This is consistent with that two different phases (HDL and LDL) that coexist in water and with the ratio of HDL to LDL changes with temperature in the supercooled region.[2]

3.2 Librational vibrations

The spectrum of HDA ice has a peak at 57 meV that is spread from 42-108 meV, and this peak is assigned to librational vibrations.[10] LDA ice and ice Ic have peaks at 67 meV that are spread from 52-118 meV. The difference between the peak energy of HDA ice and that of LDA ice shows that HDA ice has weaker hydrogen-bond interactions and therefore a longer average hydrogen-bond length than LDA ice and ice Ic.

The spectra of both LDA ice and ice Ic are cut off at 78 meV, but such a cut-off is not seen in the spectrum of HDA ice. Fukazawa *et al.*[15,21] reported that a cut-off is clearly observed in the spectrum of proton-ordered ice, ice XI, and showed that a decreasing in the number of proton configurations causes the cut-off. Thus, the number of proton configurations in HDA ice is larger than that in LDA ice and ice Ic.

3.3 Dynamical structure factor

Figure 2a and 2b show the intensity maps of $S(Q, E)$ of HDA and LDA ice (D_2O) in the ranges of Q and 0-14 $Å^{-1}$; E, 0-90 meV. The map of HDA ice shows a band of strong intensities (green color in Fig. 2a) in the Q range of 6-12 $Å^{-1}$ and E range of 38-67 meV, which are assigned to librational vibrations. Scattering due to intermolecular modes is also seen in the map as a broad band of intensities in the E range of 0-38 meV. These

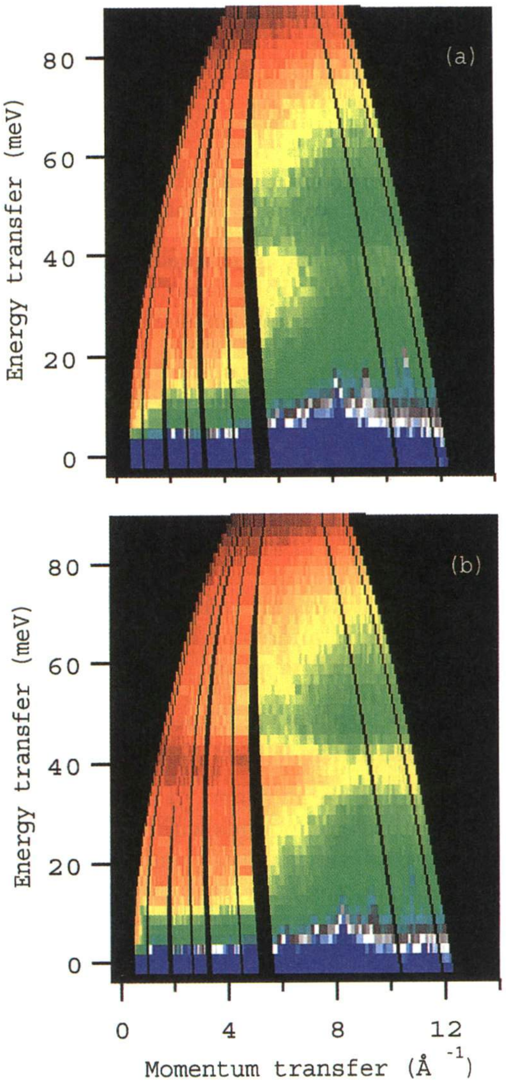

Fig. 2. Intensity maps of the dynamical structure factor, $S(Q, E)$, in (a) high-density amorphous (HDA) ice and (b) low-density amorphous (LDA) ice.

bands connect at around 8.7 Å^{-1}.

The map of LDA ice (Fig. 2b) shows a band of librational vibrations in the E range of 43-71 meV, and the value of E is larger than that in HDA ice. The larger value of E is consistent with the notion that LDA ice has stronger hydrogen-bond interactions. The scattering due to intermolecular modes is seen as a broad band of intensities in the E range of 0-32 meV. These bands are clearly separated in the E range of 32-43 meV. The results imply that the structure of LDA ice is more closely related to that of ice crystal than that of HDA ice.

§4. Conclusions

We have reported the IINS spectra of HDA and LDA ice produced by the pressurizing method. We found a clear difference between energies of 15-40 meV in HDA and LDA ice: the spectrum of HDA ice does not have any peaks, while LDA ice has two peaks at 22 and 33 meV, which are also seen in spectra of crystal ice. Thus, HDA ice contains 2-, 3-, 4-, 5-coordinated hydrogen bonds, and water molecules in which the hydrogen bond is broken migrate into the interstitial site. LDA ice contains mainly 4-coordinated hydrogen bonds. The spectrum of HDA ice is similar to the vibrational spectrum of normal liquid-water, while the structure of LDA ice is similar to that of supercooled water. This result supports the hypothesis of the coexistence of two different phases in water.[1] Furthermore, we obtained the dynamical structure factor in the amorphous ice, and showed that the structure of LDA ice is more closely related to that of ice crystal than that of HDA ice.

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