

Low-energy neutron vibrational spectra of high pressure phases of ice

A. I. KOLESNIKOV[†], J. C. LI^{‡*} and D. COLOGNESI[¶]

[†]IPNS, Argonne National Laboratory, Argonne, Illinois, IL 60439, USA

[‡]Department of Physics, The University of Manchester, Manchester M60 1QD, UK

[¶]Consiglio Nazionale delle Ricerche, Istituto di Fisica Applicata 'Nello Carrara', via Madonna del Piano, 50019 Sesto Fiorentino, FI, Italy

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An extra intensity was observed in inelastic neutron scattering spectra at low energy transfers for vapour-deposited amorphous ice and high-density amorphous (hda) ice compared to their crystalline analogues, hexagonal ice-Ih and high-pressure phase ice-VI, respectively. These low-energy excitations (LEE) in the deposited amorphous ice can be mainly described as a Boson peak. The origin of the LEE for the hda ice is not clear; it can be either due to the Boson peak or can originate from a softening of sound waves.

Keywords: Ice; Neutron spectroscopy; Boson scattering; Inelastic neutron scattering

1. Introduction

Glasses are very interesting objects in the physics of condensed matter, with many universal properties, such as the T-linear specific heat below a few K, the thermal conductivity plateau at ~ 10 K, and low-energy excitations (LEE) coexisting with the sound waves and giving an excess of vibrational modes with respect to the crystalline spectra (the so called Boson peak) in Raman and inelastic neutron scattering (INS). Recently, it was discovered in internal friction measurements that films of hydrogenated amorphous silicon do not show two-level states (TLS) effect, whereas films of amorphous silicon do [1]. Also, the resonant absorption by TLS was observed for the high-density amorphous (hda) ice but not for the low-density amorphous (lda) ice in the far infrared spectra [2]. The TLS effect in hda-ice did not show an isotope effect—it has about the same parameters for H₂O and D₂O ice forms. Using INS there a normal (Bose) temperature dependence was observed for the low-energy part of the D₂O hda-ice spectra [3], while an excess of LEE was discovered in the INS spectra for H₂O hda-ice with temperature behaviour similar to that for TLS [4]. Thus, the nature of these near universal LEE in amorphous substances becomes rather puzzling.

Essentially, two main forms of amorphous ice are known: lda-ice and hda-ice, which differ by their density, $\rho = 0.92$ and 1.17 g/cm^3 , respectively. The hda-ice can be produced by pressurising hexagonal ice-Ih at low temperature ($T < 120$ K) to a pressure above 12 kbar

*Corresponding author. Tel.: + 44-0161-200-3933. Fax: + 44-0161-200-3941. Email: j.c.li@manchester.ac.uk

[5,6], or by slowly heating the recovered high-pressure phase ice-VIII to ~ 120 K [7]. The lda-ice can be produced by heating the hda-ice to about 130 K [5,6], by hyper-quenching of water droplets of μm -size [8,9], or by low-rate water vapour deposition on a cooled substrate (vapour-deposited amorphous ice, dep-ice) [10,11]. All lda-ices have about the same density. The fundamental difference between the dep-ice and others is mainly due to the fact that for dep-ice the deposition process produces a structure with high porosity, resulting in a large number of unconnected hydrogen bonds. On the other hand, the local structures of lda-ice obtained by annealing hda-ice or by vitrification of water droplets are very similar to ice-Ih.

Earlier INS experiments with hda-ice have shown that its spectrum was very similar to that for high-pressure phase ice-VI [12–14]. Both samples were prepared by pressurising the initial ice-Ih samples to 15 kbar, at room temperature for ice-VI and at 77 K for hda-ice. The ice-VI sample was then cooled to 77 K at 15 kbar. The pressure was released and both samples were then recovered at low temperature ($T = 77$ K). Comparison of the INS spectra for the hda-ice and ice-VI revealed that both spectra have the same low-energy cut-off of the librational band, and the position of the maximum of the first acoustic peak is also at about the same energy, ~ 10 meV. At lower energies (< 8 meV) the INS spectrum for hda-ice showed an increased intensity compared to that for ice-VI.

The INS study of dep-ice [14,15] showed a softening of the librational band and an extra intensity at low energies compared to ice-Ih. The above measurements were done either with low resolution [12,13] or with good resolution but with low statistics [14,15]. Recently, INS measurements with rather good statistics and resolution have been done with D_2O hda-ice and lda-ice obtained by annealing the hda-ice [3]. The low energy part of generalised density of vibrational states, $G(E)$ obtained, for hda-ice showed a simple E^2 behaviour. However excess modes in lda-ice data were not excluded, but it was concluded that if they exist they do not lead to a clear shoulder at low energy and are difficult to distinguish from a softening of the sound-wave spectrum.

In this paper, we report the clear observation of LEE in the vibrational spectra for dep-ice as well as for hda-ice, compared to ice-Ih and ice-VI, respectively. Ice-Ih and ice-VI can be considered as being the crystalline analogues of amorphous dep-ice and hda-ice respectively, because of their similar densities.

2. Experimental details

The sample of dep-ice was prepared with a specially constructed vapour deposition centre stick for the helium cryostats used at the neutron scattering facility ISIS at the Rutherford Appleton Laboratory (UK). The water vapour was condensed on the surface of an aluminum sample-can (hollow cylinder, 60 mm long and 10 mm inner diameter), which was kept below 20 K. The temperature of water vapour at the entrance to the sample-can was 288 K, in order to avoid ice blocking the tip of the vapour jet. The deposition processes were carried out for 100 h with a flow rate of 14 mg/h. After preparation in the cryostat, the entire assembly (sample plus cryostat) was installed on the neutron spectrometer.

The hda-ice and high-pressure phase ice-VI (mass of about 1 g each) were prepared as mentioned above, by applying a pressure of 15 kbar at liquid nitrogen and room temperature, respectively. Then the pressure was released at liquid nitrogen temperature and the samples were recovered. All samples were made of double-distilled H_2O water.

The samples were loaded in a liquid nitrogen bath into a flat aluminum container (size of $2 \times 10 \text{ cm}^2$), and then into the precooled cryostats without intermediate heating, exposed at 85 K for about 20 min being pumped to remove liquid nitrogen from the sample-can, then the INS measurements were carried out at 5 K for hda-ice, ice-VI and dep-ice with the PRISMA

spectrometer [16] and at 20 K for dep-ice with the TOSCA-I spectrometer, both installed at the ISIS neutron source [17]. After the INS measurements the dep-ice samples were heated in the cryostats to 200 K (at which the dep-ice completely transforms to ice-Ih) and cooled again to the base temperature on both spectrometers. Then the INS spectra were measured for ice-Ih thus produced, at exactly the same conditions as for dep-ice. The background spectra for the empty sample-can in the cryostat were measured under the same conditions and subtracted from the original data.

The TOSCA-I and PRISMA spectrometers are inverse geometry time-of-flight machines. Neutrons from a white incident beam scattered by the sample at an angle φ with energy E_r were analyzed with a pyrolytic graphite crystal and recorded. The angle φ and energy registration E_r in the experiment were, $\varphi \approx 135^\circ$ and $E_r = 4$ meV on TOSCA-I and $\varphi = 95, 105, 115, 125$ and 135° and $E_r = 5$ meV on PRISMA. Both spectrometers provided an excellent energy resolution $\Delta E/E \approx 1-2\%$ in the range of energy transfers studied, $E = 2-150$ meV (TOSCA-I) and $E = 1-16$ meV (PRISMA), covering the range of neutron momentum transfers of $Q = 2.7-9.7 \text{ \AA}^{-1}$ and $Q = 2.4-6.2 \text{ \AA}^{-1}$, respectively.

3. Results and discussion

Figure 1 presents the spectra for dep-ice and ice-Ih measured on TOSCA-I in the range of intermolecular translational and librational vibrations of water molecules, 2–150 meV.

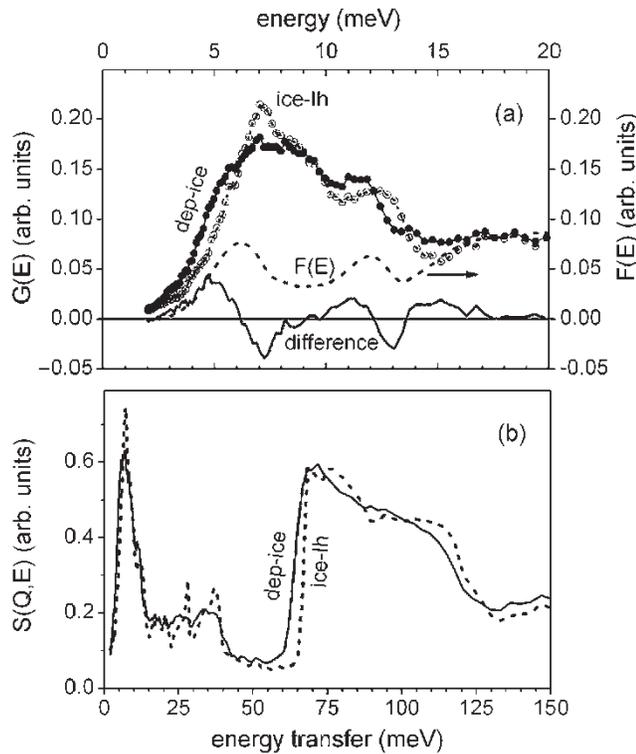


Figure 1. INS spectra for dep-ice and ice-Ih measured on TOSCA-I at 25 K: (a) $G(E)$ representation of the spectra at energy transfers below 20 meV, for dep-ice (solid curve with full points), ice-Ih (dashed curve with open points) and their difference (solid curve at the bottom). Shown also is the integrated difference of the $G(E)$ spectra as a function $F(E) = \int_0^E \Delta G(\omega) d\omega$ (dashed curve); (b) $S(Q, E)$ spectra for dep-ice (solid curve) and ice-Ih (dashed curve) at energies below 150 meV.

Shown are the dynamical structure factors $S(Q, E)$ [18], which are a standard representation of the data obtained on TOSCA-I, and low-energy generalized density of vibrational states $G(E)$, which is in some degree a “spectrometer and temperature” independent representation of the vibrational spectra and can be expressed by the following transformation:

$$G(E) \propto S(Q, E) \frac{E}{Q^2 [n_B(E) + 1]}, \quad (1)$$

where $n_B = [\exp(E/k_B T) - 1]^{-1}$ is the Bose factor and T is temperature.

The $S(Q, E)$ and $G(E)$ data in the range of the acoustic peak 1–15 meV for dep-ice and ice-Ih, and for hda-ice and ice-VI obtained on PRISMA are shown in figure 2. They are of a rather high accuracy at low-energy transfer because PRISMA has a very low background around the elastic line, compared to other spectrometers. Figures 1 and 2 also show the difference spectra between the amorphous forms and their crystalline analogues.

It is clearly seen from figure 1 that a strong softening by about 3.5 meV of the low-energy cut-off of the librational band (around 65 meV) occurs for dep-ice compared to ice-Ih, which is in accord with our previous measurements [14,15]. This reflects the fact that intermolecular transverse forces for dep-ice are weaker than for ice-Ih, which can be understood by supposing that large amounts of hydrogen bonds between water molecules in dep-ice are broken. The two very sharp optical peaks in the translational part of the spectrum for ice-Ih (with maxima at 28 and 38 meV) appear as smooth humps for the dep-ice spectrum.

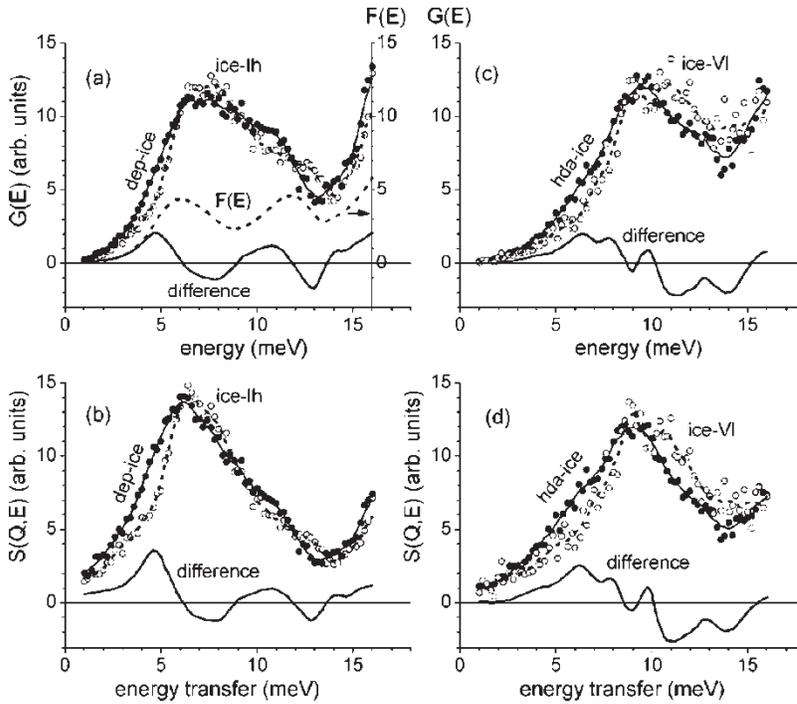


Figure 2. INS spectra (below 16 meV) measured on PRISMA at 5 K for dep-ice (solid curve with full points) and ice-Ih (dashed curve with open points), (a) and (b) at the left, and for hda-ice (solid curve with full points) and high-pressure phase ice-VI (dashed curve with open points), (c) and (d) at the right. Shown are $G(E)$ and $S(Q, E)$ representations of the spectra at the top (a) and (c), and at the bottom (b) and (d) of the figure, respectively. Solid curves on the figure marked as “difference” are the differences between the corresponding spectra. The integrated difference of the $G(E)$ spectra for dep-ice and ice-Ih as a function $F(E) = \int_0^E \Delta G(\omega) d\omega$ is shown in part (a) by dashed curve.

The disappearing of the sharp structures in the spectrum for dep-ice is due to structural disorder in amorphous ice, and thus larger a distribution of the potential field for water molecules.

The figures 1(a) and 2(a) show that the acoustic peak in the $G(E)$ spectra for dep-ice has smaller intensity at its maximum but an extra intensity is seen at the low- and high-energy sides of the peak. So it could be considered that the acoustic peak for dep-ice is not simply softer compared to ice-Ih, but it has an extra intensity on both sides of its maximum. The Debye-Waller (DW) factor in the $G(E)$ representation obtained by equation (1) was not taken into account. The correction for DW factor at low energies will only slightly increase the intensity of the spectrum for the amorphous sample due to the larger mean-squared displacements of the atoms/molecules in the amorphous state compared to the crystalline one.

The integrated intensity of the acoustic peak for dep-ice measured at TOSCA-I (1–15 meV) is also noticeably larger compared to that for ice-Ih by about 5.8 and 3.7% for $S(Q, E)$ and $G(E)$ representations, respectively. The corresponding values for the spectra obtained at PRISMA are 7.7 and 4.1%. Note once again that the sample was transformed from its amorphous state to the crystalline one at the spectrometer, so both states of the sample were measured under exactly identical conditions. No reasonable explanation, except for the Boson peak, exists now for the observed extra intensity in the $G(E)$ spectra for amorphous deposited ice compared to ice-Ih, which amounts to about 5% of the total intensity of the acoustic peak (at energies $E < 15$ meV) and more than 30% at energies below 6 meV (under the first peak in the $\Delta G(E) = G^{\text{dep-ice}}(E) - G^{\text{ice-Ih}}(E)$ difference

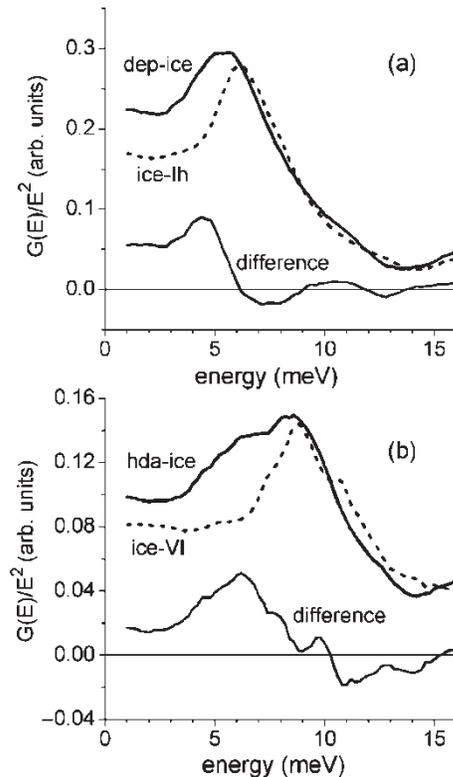


Figure 3. $G(E)/E^2$ dependencies for: (a) dep-ice (solid curve), ice-Ih (dashed curve) and their difference (solid curve at the bottom); and (b) hda-ice (solid curve), ice-VI (dashed curve) and their difference (solid curve at the bottom). Data obtained from INS spectra measured on PRISMA.

spectrum). To emphasize the existence of the extra intensity for the acoustic part of the dep-ice spectrum the integrated difference of the $G(E)$ spectra are also plotted in figures 1(a) and 2(a) as a function

$$F(E) = \int_0^E \Delta G(\omega) d\omega. \quad (2)$$

The short dashed curves for $F(E)$ in the figures evidently show that this function never goes to zero in the range of the acoustic peak. The simple softening of the acoustic peak in the amorphous state would give a zero value for the integrated difference $\Delta G(E)$ under the acoustic peak area, which clearly is not the case in the present study. Thus, in addition to a possible softening of the acoustic modes due to the reduction of intermolecular forces in the disordered systems the extra intensity at low energies (around 5 meV) in the INS spectra for dep-ice can be essentially called the Boson peak.

The spectra for hda-ice and ice-VI were normalized to their areas, because the exact masses of the samples in the neutron beam were not known (while it was exactly the same in the case for dep-ice and ice-Ih measurements). The acoustic spectra for hda-ice and ice-VI show the same position for their maxima, at ~ 9 meV, with an extra intensity on the low-energy side (below 8.5 meV) and a deficit of intensity at the high-energy side (above 10 meV) of the peak for hda-ice (figure 2(c),(d)).

All the spectra studied here exhibit a Debye-law behaviour for their low energy part, $G(E) \sim E^2$, but the energy range of this dependence is larger for crystalline ices compared to amorphous ones. Figure 3 shows the $G(E)/E^2$ representation of the spectra and their differences, where one can see a constant-like behaviour at energies below ~ 3 meV for both amorphous ices and below about 4.5 and 6.5 meV for ice-Ih and ice-VI, respectively. These values show the range of validity of the “pure” sound-wave nature of the excitations in the studied ices.

Due to normalization uncertainties for hda-ice and ice-VI data, it is difficult to decide from the obtained data if the extra intensity at low energy of $G(E)$ spectrum for hda-ice is due to the Boson peak or due to a simple softening of the acoustic peak, compared to ice-VI. But in any case, the Debye-law behaviour for hda-ice exists at a much smaller energy range compared to its crystalline analog ice-VI.

4. Conclusion

INS spectra were measured for two amorphous ices, dep-ice and hda-ice, and their crystalline analogues, ice-Ih and ice-VI. In addition to a possible softening of the acoustic modes due to the reduction of intermolecular forces in the disordered systems, the comparison of the spectra for dep-ice and ice-Ih (obtained at exactly the same conditions) indicates the existence of a Boson peak at energies around 5 meV for dep-ice. The low-energy extra intensity in the spectrum of hda-ice compared to ice-VI could be either due to the Boson excitations or due to the softening of the acoustic peak. For both amorphous ices the $G(E) \sim E^2$ dependence is valid for a smaller energy range compared to their crystalline analogues.

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