ANL/IPNS/CP-96860
Submitted to The Ninth International Conference on Phonon Scattering in Condensed Matter, 26-31 July 1998, Lancaster, U

15 June, 1998

Neutron spectroscopy of high-density amorphous ice

A.I. Kolesnikov[a], J.C. Li[a], N.C. Ahmad[b], C.-K. Loong[c], J. Nipko[c], D. Yocum[c] and S.F. Parker[d]

[a]*Department of Physics, UMIST, PO Box 88, Manchester, M60 1QD, UK*

[b]*The University of Surrey, Guildford, Surrey GU2 5XH, UK*

[c]*Argonne National Laboratory, Argonne, IL 60439-4814, USA*

[d]*ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon, OX11 0QX, UK*

Abstract

Vibrational spectra of high-density amorphous ice (hda-ice) for H_2O and D_2O samples were measured by inelastic neutron scattering. The measured spectra of hda-ice are closer to those for high-pressure phase ice-VI, but not for low-density ice-Ih. This result suggests that similar to ice-VI the structure of hda-ice should consist of two interpenetrating hydrogen-bonded networks having no hydrogen bonds between themselves.

Keywords: amorphous ice, neutron spectroscopy

Corresponding author: A.I. Kolesnikov, Department of Physics, UMIST, PO Box 88, Manchester, M60 1QD, UK; Fax: 44 (0) 161 200 3941; e-mail: A.Kolesnikov@umist.ac.uk

DISCLAIMER

One of the interesting results from investigations of the structure and dynamics of ice was the observation of the phase transition from hexagonal ice-Ih to high-density amorphous (hda) ice by applying a pressure of ~10 kbar at low temperatures (T<130 K) [1]. The density of hda-ice (~1.31 g/cm^3 at 10 kbar) is about 40% higher than that of ice-Ih (0.94 g/cm^3 at ambient pressure). The inelastic neutron scattering (INS) spectrum of hda-ice H_2O in the range of the intermolecular vibrations (2 to 200 meV) was studied recently [2,3]. In the present report, we extended the INS investigations of the recovered hda-ice to its deuterated form and isotope mixture in the range of intermolecular vibrations, as well as for H_2O ice in the range of the intramolecular bending and stretching modes.

The INS spectrum for D_2O hda-ice in the range of intermolecular vibrations measured on TFXA spectrometer [4] is shown in the Fig. 1. The data are compared with the spectra for low-density "normal" ice-Ih and high-pressure phase ice-VI, measured previously [5]. It is obvious from the figure that the spectrum for hda-ice D_2O is similar to that for ice-VI. In the Fig. 2 the INS spectrum for hda-ice D_2O is compared with the spectrum for protonated hda-ice, H_2O. The translational parts of the spectra (below 40 meV) look identical. The librational band for H_2O ice, after the energy is scaled by the square-root of the ratio of the moments of inertia for the corresponding water isotopomers ($\sim\sqrt{2}$), coincides with that of D_2O, indicating a rather harmonic behaviour of the librational band.

Fig. 3 shows the INS spectrum for H_2O hda-ice obtained on the HERMECS spectrometer [4] in the energy range up to 450 meV. The comparison with the spectra for ice-Ih and ice-VI [6] (also shown in the figure) clearly indicates the similarity of the bending and stretching modes for hda-ice and ice-VI. Surprisingly, the stretching mode peak for hda-ice looks narrower than for the crystalline phase ice-VI.

The INS spectrum for the water isotope mixture $(D_2O)_{0.9}(H_2O)_{0.1}$ for hda-ice measured on HERMECS and for ice-Ih measured on HET earlier [8] are shown in the Fig. 4. The hydrogen defect mode peak (around 100 meV) for hda-ice is noticeably broader and seen at much lower energy.

The strong softening of the intermolecular librational band and hydrogen defect mode peak and the hardening of the intramolecular stretching modes in the hda-ice compared to ice-Ih indicate that the oxygen-oxygen separation distances in hda-ice are longer than in low-density ice-Ih. The similarity of the INS spectra for hda-ice and ice-VI over the whole range of the intermolecular and intramolecular vibrations suggests that the forces between water molecules and the local molecular arrangements for these ices are rather similar. Thus, similar to ice-VI, the structure of hda-ice is proposed to consist of two interpenetrating hydrogen-bonded networks having no hydrogen bonds between the networks.

Acknowledgments

We thank the EPSRC for access to the ISIS pulsed neutron source. Work performed at Argonne is supported by the U.S. DOE-BES under contract No. W-31-109-ENG-38.

References

[1] O. Mishima, L.D. Calvert and E. Whalley, Nature 310 (1984) 393; and 314 (1985) 76.

[2] A.I. Kolesnikov et al., J. Phys.: Condens. Matter 6 (1994) 375.

[3] J.C. Li, J. Chem. Phys. 105 (1996) 6733.

[4] 1992 ISIS User Guide to Experimental Facilities, SERC, eds. B. Boland and S. Wapham, 75 pp.

[5] J-C. Li et all., J. Chem. Phys. 94 (1991) 6770.

[6] IPNS Progress Report 1991-1996, Vol. 1, ed. B. Morzec, (Argonne National Laboratory, 1996) 168 pp.

[7] J-C. Li et all., J. Phys.: Condens. Matter 4 (1992) 2109.

[8] J-C. Li and D.K. Ross, J. Phys.: Condens. Matter 6 (1994) 10823.

Figure captions

Fig. 1. The INS spectra (D_2O) in the range of the intermolecular vibrations for hda-ice and ice-VI and ice-Ih measured on TFXA. The smoothed curves for hda-ice and ice-VI are shown superimposed for better visual comparison in part (a) of the figure.

Fig. 2. The INS spectra for hda-ice H_2O and D_2O. The solid curve plotted over the D_2O data is the spectrum for H_2O sample, energy scaled by $\sqrt{2}$ ($E=E/\sqrt{2}$).

Fig. 3. The INS spectra (H_2O) for hda-ice measured on HERMECS, and for ice Ih and ice-VI measured on HET [6] in the energy range up to 450 meV (including intramolecular vibrations).

Fig. 4. The INS spectra for $(D_2O)_{0.9}(H_2O)_{0.1}$ measured on HERMECS for hda-ice and on HET for ice-Ih [7]. The solid curves are the polynomial smoothed data.

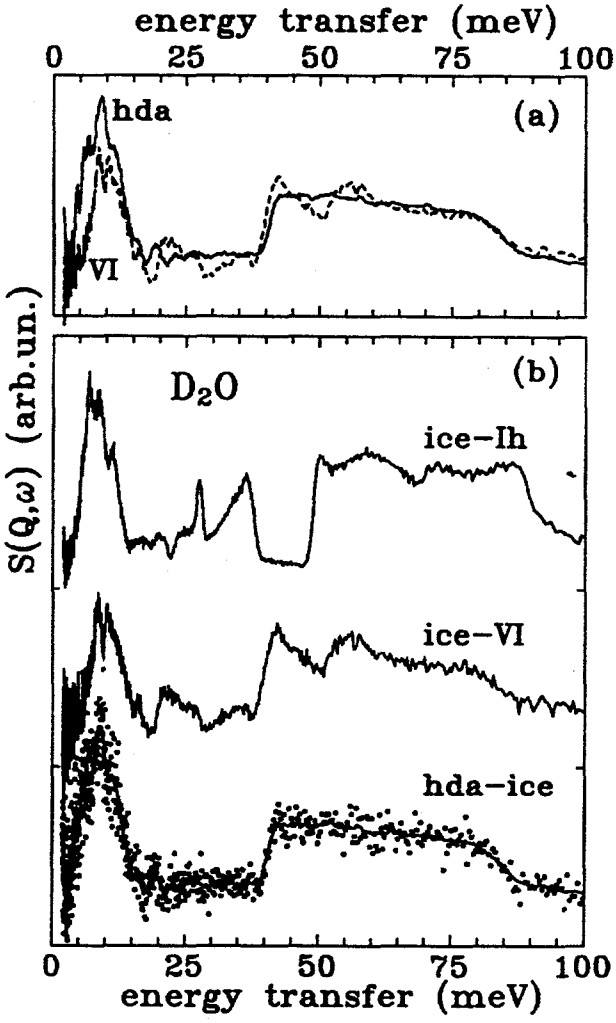
energy transfer (meV)
0
25
50
75
100
hda
(a)
VI
S(Q,ω) (arb.un.)
D2O
(b)
ice-Ih
ice-VI
hda-ice
0
25
50
75
100
energy transfer (meV)

Fig. 1

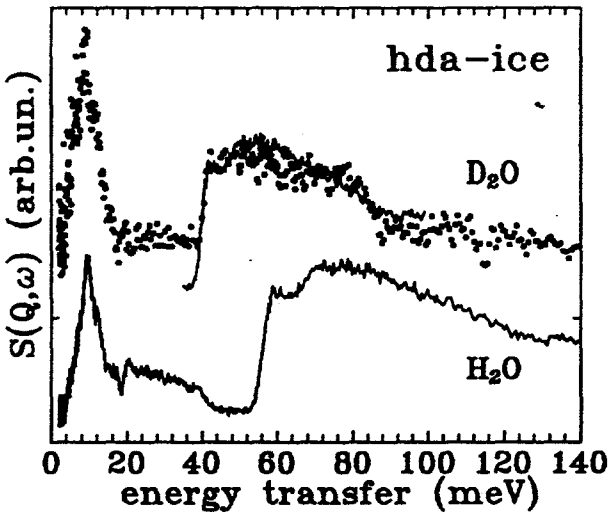
hda–ice
D_2O
H_2O
S(Q,ω) (arb.un.)
0 20 40 60 80 100 120 140
energy transfer (meV)

Fig. 2

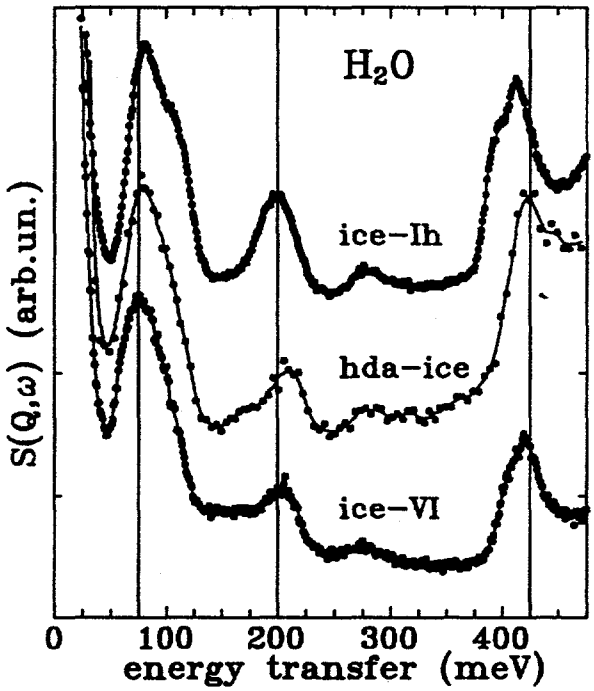
H2O
ice–Ih
hda–ice
ice–VI
S(Q,ω) (arb.un.)
0
100
200
300
400
energy transfer (meV)

Fig. 3

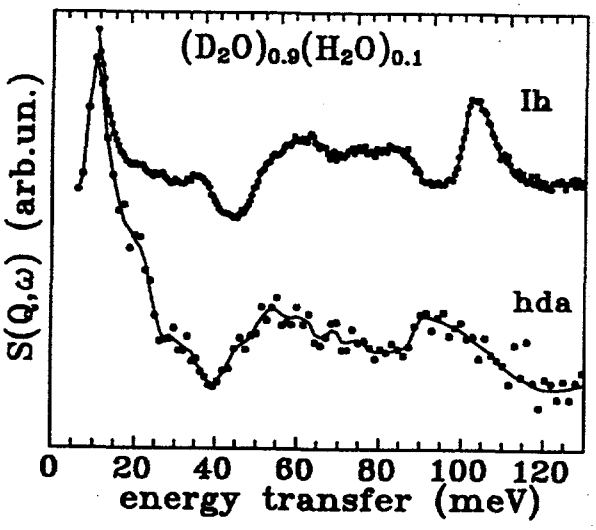
$(D_2O)_{0.9}(H_2O)_{0.1}$
Ih
hda
S(Q,ω) (arb.un.)
0
20
40
60
80
100
120
energy transfer (meV)

Fig. 4