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Densities of vibrational states and heat capacities of crystalline and amorphous H_2O ice determined by neutron scattering

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The densities of vibrational states $g(\nu)$ of crystalline ice Ih and Ic, and of low-density and high-density amorphous ice, all at 15 K, have been determined by incoherent inelastic neutron scattering. The use of a self-consistent iterative procedure to correct for multiphonon and multiple scattering leads to highly accurate values. The mean absolute difference for $T < 80$ K between the heat capacity of ice Ih calculated from our $g(\nu)$ and that measured calorimetrically is 1.8%. The anharmonic component of the heat capacity at higher T is about twice as large as an earlier theoretical estimate.

Incoherent inelastic neutron scattering (IINS) is a potentially powerful method for determining the density of vibrational sates, or frequency distribution function, $g(\nu)$, of crystals and amorphous solids, but various difficulties in analysis have often limited the accuracy of the $g(\nu)$ values thus obtained, particularly for molecular solids.[1] The most serious difficulties are accurately correcting for multiphonon and multiple scattering, and determining the separate contributions from translational, librational, and internal vibrational modes in cases where they overlap and mix. In addition to being of high intrinsic interest, the many crystalline and amorphous phases of ice provide excellent systems for testing methods of analyzing IINS data because the dominant contribution to the scattering is the incoherent scattering by hydrogen, and because, as shown by our new results for all four phases, and inferred[2] earlier for ice I from optical spectroscopy, the translational and librational bands do not overlap. These advantages greatly simplify the data analysis. The various phases of ice are chemically identical but cover a wide range of densities, giving rise to marked differences in $g(\nu)$. In particular, high-density amorphous (hda) ice, as made by compressing ice I to 10 kbar at 77 K and recovering it at 1 bar and 77 K, is[3] about 25% denser than ice I. Structural studies by diffraction,[4-6] vibrational spectroscopy,[7] and theory[8] have suggested that hda ice is closely related to the glass that would be obtained if water could be quenched at 10 kbar, and its properties, as well as the exact nature of the transformation of ice I to hda ice, are of high current interest.[9,10]

In this paper we report the determination of $g(\nu)$ for cubic (Ic) and hexagonal (Ih) ice, low-density amorphous (lda) ice, and hda ice by IINS. These are the first experimental determinations of $g(\nu)$ for ice Ic and for lda and hda ice. Our highly accurate $g(\nu)$ values, which result from extensive data correction procedures, taken together with calorimetric values of the total heat capacity of ice Ih, which are known[11] to ±1%, allow us to make the first experimental determination of the anharmonic component of the heat capacity.

The sample of hda ice, 69.5 mm in diameter and 2 mm thick, was made by compressing ice Ih in a piston-cylinder apparatus to 13 kbar at 77 K. It was recovered at 1 bar and 77 K, sandwiched between two silicon single-crystal wafers in an aluminum holder, mounted on the cold finger of a CTI CRYOGENICS closed-cycle refrigerator, and cooled to 15 K for the neutron-scattering measurements. The lda, Ic, and Ih phases were made by annealing, successively, at 115, 155, and 240 K. Each successive phase was cooled to 15 K for the neutron-scattering measurements and, finally, the scattering at 15 K by the empty cell was also determined. We were thus able to make measurements on all four phases using a single sample. The neutron-inelastic-scattering measurements were done on the *N*5 triple-axis spectrometer at Chalk River with the sample in symmetric transmission. A silicon (331) monochromator and a silicon (111) analyzer were used. The wave-vector transfer Q was 6.0 Å^{-1} and the scattered-neutron frequency was fixed at 8 THz. The frequency transfer ν covered the range -0.8 to 31.4 THz with the frequency resolution (FWHM) varying from 0.5 to 2 THz over this range.

The incoherent scattering function of a harmonic crystal is uniquely determined[12] by the velocity spectrum $f(\nu)$ which, for a cubic Bravais lattice, is simply the density of states $g(\nu)$. For ice,

$$g(\nu)=g_t(\nu)+g_l(\nu)\ , \tag{1}$$

where the subscripts t and l label the translational and librational bands which have equal integrated intensities and, as we shall see, do not overlap. The velocity spectrum can be decomposed in an analogous way, and Prask *et al.*[13] have calculated that in harmonic ice Ic the ratio $f(\nu)/g(\nu)$ is almost constant over both the translational and librational bands. In other words,

$$f(\nu)=2(1-x)g_t(\nu)+2xg_l(\nu)\ , \tag{2}$$

where x is approximately constant and represents the relative intensity of the librational band. Assuming that (2) is valid, in general, for ice, we find that $x=0.91$ for all four phases that were studied, in good agreement with the value 0.86 calculated by Prask *et al.*[13] In order to obtain $f(\nu)$, the observed scattering must be corrected for several effects. Corrections were first made for the scattering by the empty cell, the elastic scattering by the ice, and the measured inhomogeneity of the flux distribution in the incident beam. The absorption, self-shielding, multiphonon scattering, and multiple scattering were then calculated using an iterative procedure. This procedure is partly based on a straightforward application of the well-known multiphonon expansion[14] of the incoherent scattering function, in which the n-phonon contribution is given by a convolution of the one-phonon and the $(n-1)$-phonon contributions, and was performed self-consistently starting from an assumed initial $f(\nu)$ distribution.[15] Contributions from up to six-phonon processes were included. Higher-order processes contribute less than 0.1% to the multiphonon scattering. The multiple scattering was calculated using the method of Sears.[16] Essentially perfect agreement with the observed net inelastic scattering was achieved after four iterations. Rapid convergence was achieved because the multiphonon scattering is not very sensitive to the detailed shape of $f(\nu)$.

In Fig. 1 we show the net inelastic scattering by lda ice and its decomposition into one-phonon, multiphonon, and multiple-scattering components. Note that the multiphonon scattering, about 15 and 35 % of the total intensity in the translational and librational bands, respectively, exhibits considerable structure and, together with the multiple scattering, accounts entirely for the observed intensity in the region between the two bands. Similar decompositions were obtained for the other phases; that for ice Ic was shown in an earlier Brief Report[17] on this work. Li *et al.*[18] have recently reported neutron-scattering measurements on ice Ih. Their results for the total inelastic scattering are very similar to ours but they have not carried out corrections for multiphonon and multiple scattering in order to obtain experimental $g(\nu)$ values.

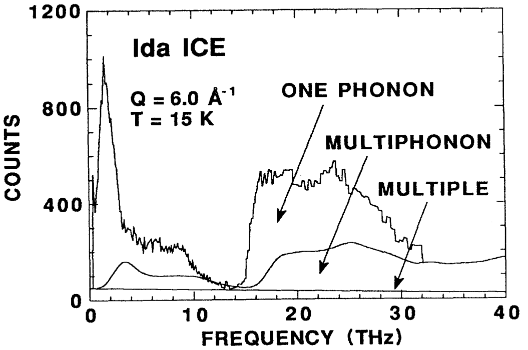

FIG. 1. The net inelastic scattering by lda ice and its decomposition into one-phonon, multiphonon, and multiple-scattering components.

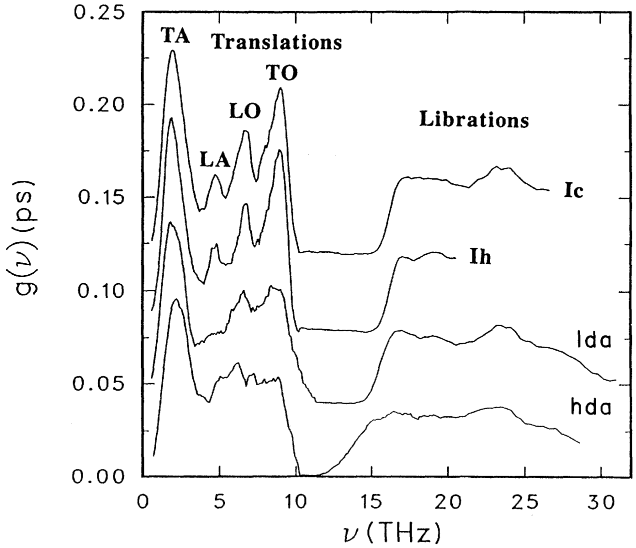

FIG. 2. Densities of states $g(\nu)$ for four phases of H_2O ice. Five-point smoothing has been used. The assignments in the translational region are those of Prask *et al.* (Ref. 13); TA, LA, LO, and TO refer to transverse and longitudinal acoustic and optic branches of the dispersion relation. The values for lda ice, ice Ih, and ice Ic are shifted upwards by 0.04, 0.08, and 0.12 ps, respectively.

The one-phonon contribution in Fig. 1 is proportional to $f(\nu)$. The corresponding $g(\nu)$ determined from (1) and (2) is shown in Fig. 2 together with those for the other three phases. Earlier experimental determinations[13,19] of $g(\nu)$ for ice Ih exhibited features qualitatively similar to those in Fig. 2 but the structure is considerably sharper in our work, the relative intensities of the different features are greatly different, and we observe, for all phases, a clear separation of the translational and librational bands which was not evident in the earlier studies. As was largely to be anticipated, we find that $g(\nu)$ for ice Ic is essentially identical to that for ice Ih. The TA peak is very similar in all four phases, but the structure at higher ν in the translational band becomes progressively more washed out and weighted to lower ν as one moves from ice I to lda and hda ice. Note, however, that the translational band extends to about 10 THz in all phases, even slightly higher in lda ice, which indicates that the long-range dipolar forces known[20] to be responsible for the higher-frequency translational modes in ice I are equally important in the amorphous phases. The leading edge of the librational band begins at much lower ν and rises much more slowly in hda ice than in ice I. This behavior is undoubtedly a reflection of the fact that, in spite of the much higher density, the mean hydrogen-bonded O-H—O length is actually greater in hda ice than in ice I, and the distribution of bond lengths is much broader.[7] The onset frequency of about 12 THz in hda ice corresponds to a hydrogen-bond that is about 0.18 Å longer than the mean length of 2.76 Å in ice Ih. This agrees well with the upper limit of the distribution of hydrogen-bond lengths in hda ice found by Raman spectroscopy.[7] To a much lesser extent, the leading edge of the librational band for lda ice also starts at lower ν and rises more gently than for ice Ic, again in agreement with what is known[7] about the bond lengths.

The $g(\nu)$ values from the present work, which are essentially those for $T=0$, can be used to calculate the harmonic heat capacity. Comparison with the experimental heat capacity from calorimetric measurements then provides a test of the accuracy of the $g(\nu)$ values. The harmonic heat capacity at constant volume, C_v^{har}, is given by

$$C_v^{\text{har}}=6R\int_0^\infty \frac{(h\nu/kT)^2 e^{-h\nu/kT} g(\nu)}{(1-e^{-h\nu/kT})^2}\,d\nu\ , \tag{3}$$

where R, h, and k are, respectively, the gas, Planck, and Boltzmann constants. C_v^{har} is related to the heat capacity at constant pressure, C_p, by the equation

$$\Delta C \equiv C_p - C_v^{\text{har}} = TV\alpha^2/\beta + \Delta C_v^{\text{anh}}\ , \tag{4}$$

where α is the volume thermal expansivity, β the isothermal compressibility, V the molar volume at temperature T, and ΔC_v^{anh} is the anharmonic heat capacity at constant volume. The C_v^{har} values for the four phases of ice calculated from (3) are shown by solid curves in Fig. 3. The effect of different truncations of $g(\nu)$ at high ν in Fig. 2, all chosen, of course, to give the same integrated area under $g(\nu)$ for the translational and librational bands, is to alter C_v^{har} by less than 0.1% at 200 K. The dashed curves for ice Ih and Ic are the calorimetric C_p values of Haida *et al.*[11] and Flubacher *et al.*[21] for ice Ih which are assumed to be appropriate for both phases since, as we have seen in Fig. 2, their $g(\nu)$ values are essentially identical, as are their infrared and Raman spectra.[22] The mean absolute deviation of the calorimetric heat capacity from that given by (3) up to 80 K is 1.8% for ice Ih. This superb agreement, essentially at the level of accuracy of the calorimetric C_p values, confirms the high accuracy of our $g(\nu)$ values. In the pioneering work of Boutin and Yip[1] and Prask *et al.*[19] deviations as large as 25% between C_p and C_v^{har} were obtained unless an almost complete overlap of the translational and librational bands was assumed. This is not consistent with our observations. We have thus decreased the deviations by more than an order of magnitude and demonstrated that it is possible to almost completely overcome the difficulties identified in the early studies.[1,19] It should be noted that the early lattice dynamical model of Prask *et al.*[13] for ice Ic gave good agreement with the measured heat capacity of ice Ih but, in contrast, this was not a calculation using experimental $g(\nu)$ values as in the work presented here.

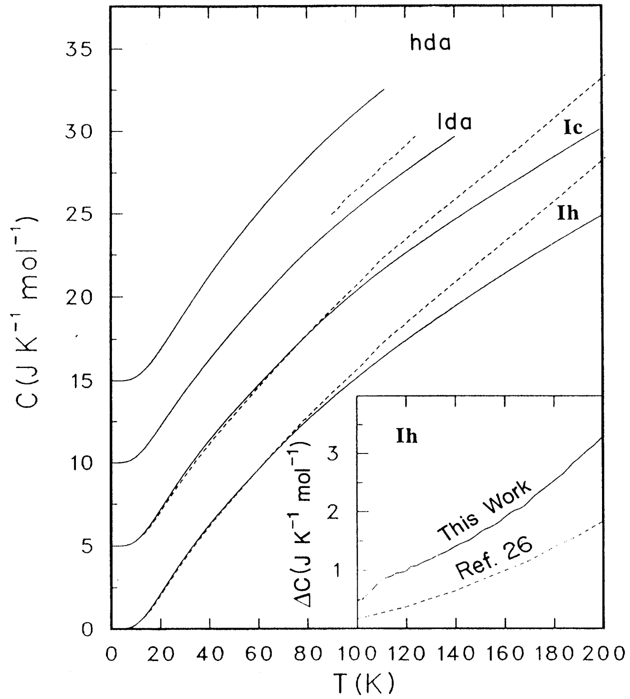

FIG. 3. The harmonic heat capacities C_v^{har} of four phases of ice calculated from our $g(\nu)$ values (——) and the corresponding calorimetric C_p values (— — —) for lda ice (Ref. 27) and ice Ih (Refs. 11 and 21), also assumed to be appropriate for ice Ic. The heat capacities of ice Ic, lda ice, and hda ice have been shifted upwards by 5, 10, and 15 J K^{-1} mol^{-1}, respectively. The anharmonic heat capacity ΔC of ice Ih, defined by (4), is compared with the theoretical result of Leadbetter (Ref. 26) in the inset.

The excellent agreement for $T<80$ K in Fig. 3 suggests that the harmonic heat capacity of ice I can be accurately calculated at higher temperatures, and that that of lda and hda ice can be accurately predicted. The first term on the right-hand side of (4) was evaluated from known values of V (Ref. 23), α (Ref. 24), and β (Ref. 25). It increases from 0.025 J K^{-1}mol^{-1} at 100 K to 0.370 J K^{-1}mol^{-1} at 200 K. Therefore, the anharmonic heat capacity at constant volume increases from 0.47 to 2.8 J K^{-1}mol^{-1} over the same temperature range, and is clearly the dominant contribution to the anharmonic component of the heat capacity, as suggested by Leadbetter's calculations.[26] The total anharmonic heat capacity of ice Ih from the present work, which is the first experimental determination of this quantity, is seen from the inset in Fig. 3 to be about twice as large as Leadbetter's theoretical estimate. The calorimetric heat capacity of lda ice[27] (dashed curve in Fig. 3) is about 6% higher than C_v^{har} at 100 K, a difference about three times larger than for ice I. The anharmonic contribution is thus much larger in lda ice than in ice I. One might expect an even larger anharmonic contribution for hda ice because of a larger number of low-frequency modes but, unfortunately, calorimetric C_p values to compare with our C_v^{har} values do not yet exist for this phase. It would clearly be very valuable to have such results for hda ice as well as additional results at lower T for the form of lda ice obtained by transforming hda ice.

In summary, we have obtained $g(\nu)$ values for two crystalline and two amorphous phases of ice. These $g(\nu)$ values are sufficiently accurate to provide benchmarks for the testing of intermolecular potentials in the solid phases of water as well as the testing of models for the structure of the amorphous phases. Their high accuracy has allowed us to make the first experimental determination of the anharmonic contribution to the heat capacity of ice Ih which we find to be about twice as large as had been predicted. The methods of analysis are, in principle, applicable to any molecular solid although there will, of course, be additional complications for materials where different vibrational bands strongly overlap.

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