Crystal-like High Frequency Phonons in the Amorphous Phases of Solid Water

H. Schober,[1] M. M. Koza,[2,1] A. Tölle,[2] C. Masciovecchio,[3] F. Sette,[4] and F. Fujara[5]

[1]*Institut Laue-Langevin, F-38042 Grenoble Cedex, France*
[2]*Fachbereich Physik, Universität Dortmund, D-44221 Dortmund, Germany*
[3]*Sincrotrone Trieste, Area Science Park, I-34017, Trieste, Italy*
[4]*European Synchrotron Radiation Facility, B.P. 220, F-38043 Grenoble Cedex, France*
[5]*Fachbereich Physik, Technische Universität Darmstadt, D-64289 Darmstadt, Germany*

(Received 25 February 2000)

The high frequency dynamics of low-density (LDA) and high-density (HDA) amorphous ice and of cubic ice (I_c) has been measured by inelastic x-ray scattering in the $1-15$ nm^{-1} momentum transfer (Q) range. Sharp phononlike excitations are observed, and the longitudinal acoustic branch is identified up to $Q = 8$ nm^{-1} in LDA and I_c and up to 5 nm^{-1} in HDA. The narrow width of these excitations is in sharp contrast to the broad features observed in all amorphous systems studied so far. The "crystal-like" behavior of amorphous ices, therefore, implies a considerable reduction in the number of decay channels available to soundlike excitations which is interpreted as a sign of low local disorder.

PACS numbers: 63.50.+x, 64.70.Kb, 78.70.Ck

Amorphous polymorphism, i.e., the existence of two or more amorphous states in the phase diagram of a chemical substance, has recently attracted wide interest from the scientific community [1]. In water, amorphous polymorphism has received particular attention as it was associated with a possible phase separation in the deeply undercooled liquid [2]—this is suggested by the idea that the two amorphous water phases may be identified with the glassy forms of two liquid phases. In systems such as water, the ergodic to nonergodic transition from the undercooled liquid to the glass cannot be studied continuously as a function of temperature due to homogeneous crystallization. The glassy nature of the amorphous ice phases can, therefore, only be established indirectly, and this has contributed in raising controversies on the exact nature of the phase diagram of water, and on the interrelations among the different stable and metastable phases of this molecule [3].

The growing perception that the glassy state is a very general state of condensed matter justifies the many experimental, theoretical, and simulation studies performed on glasses. Among them, there is a growing interest in the study of the collective dynamical properties at high frequency, i.e., in the wavelength regime approaching the interparticle distances. Here one expects that either a continuum description, valid in the hydrodynamic limit, or the ordered-medium (phonon) picture developed for crystalline materials will fail as a consequence of the disorder. The deviations can then be used to characterize and better understand the glassy state. More specifically, there is a number of dynamic signatures which are associated with the glassy state [4]. Disorder scattering and anharmonicities lead to excess densities of states (Boson peak) and relaxational phenomena [5]. Recently, the overdamping of sound waves at high frequency was proposed as a further criterium to characterize the glassy behavior [6]. Both the Boson peak and the overdamping behavior have been correlated with the fragility of a glassy system. Based on systematic comparisons it is conjectured that the stronger the glass the more pronounced are these typical dynamic signatures [6,7]. The study of the collective dynamics of amorphous ice at wavelengths approaching the distance among water molecules may contribute, therefore, to the understanding of the differences between these two phases, and may help to shed light on such issues as their relation to stable crystalline phases or on the existence of two different liquid phases.

In this Letter we present the excitation spectrum of both amorphous forms of water, i.e., high-density (HDA) and low-density (LDA) amorphous ice, as determined by high resolution inelastic x-ray scattering (IXS) at momentum transfers (Q) comparable to the inverse of the intermolecular distance. The experiment has been performed at the very high energy resolution beam line ID16 at the European Synchrotron Radiation Facility in Grenoble. The instrument energy resolution was set to 1.6 meV full width at half maximum (FWHM) using 21.748 keV incident photons. Further experimental details can be found elsewhere [8].

The HDA sample was obtained by pressurizing hexagonal D_2O ice I_h at 77 K [9] beyond 10 kbar using the piston-cylinder apparatus described previously [10]. The metastable compound was retrieved from the pressure cell at ambient pressure and 77 K in mm-size chunks ($\rho = 1.17 \pm 0.02$ g/cm^3) and transferred onto the cold finger of a precooled closed-cycle refrigerator. The effective sample thickness along the beam was $\approx$15 mm, matching well the x-ray photoabsorption length. Above $\approx$90 K HDA transforms with a strongly temperature dependent rate to LDA ($\rho = 0.94 \pm 0.02$ g/cm^3), which, in turn, converts itself into cubic ice I_c at $\approx$140 K. HDA and LDA, after proper annealing, were both measured at 60 K, while I_c after annealing was measured at 80 K. The similarity of the temperatures allows a direct comparison of the scattering intensities.

 0031-9007/00/85(19)/4100(4)$15.00

The purity of each phase was checked by measuring the respective static structure factors, $S(Q)$, reported in Fig. 1 with a momentum resolution of 0.04 nm^{-1} and by taking x-ray photographs. Both HDA and LDA samples show the known static structure factor [11]. No signs of Bragg peaks (Fig. 1) or Debye-Scherrer rings (x-ray photographs) are observed and, therefore, the samples are free of crystalline ice XII [12,13]. There is a pronounced small-angle signal in HDA which disappears upon annealing to LDA. Within our energy resolution, its origin is purely elastic as will be seen by the inelastic scans reported in the following. As only moderate changes in the elastic small angle signal were observed with neutrons [10], it is questionable whether the strong effect observed here is a real bulk property of the HDA sample or whether its origin stems from surface scattering in the powder sample.

Selections of inelastic spectra are reported in Figs. 2 and 3. In both amorphous ice phases and in the cubic crystalline phase there are well-pronounced resonances. In order to derive the energy position, $\hbar\Omega(Q)$, and the width, $\hbar\Gamma(Q)$, of the excitations, they have been fitted by various model functions. They all give similar results. We, therefore, present only the analysis in terms of Lorenzian functions convoluted with the experimentally determined instrument resolution. This resolution function corresponds to the central peak at $E = 0$ in Figs. 2 and 3 that, as discussed previously, is due to the static disorder in the samples and to small angle scattering from the sample environment (see Ref. [8]). The fits give excitation energies $\hbar\Omega(Q)$ which scale linearly with the momentum transfer Q in the limit of small Q (Fig. 4). As x rays, like neutrons, couple directly to the longitudinal component of the density fluctuations, the excitations can be readily identified with the longitudinal acousticlike branches. The sound velocities are $c_{\mathrm{HDA}} = 3550 \pm 50$ m/s, $c_{\mathrm{LDA}} = 3550 \pm 50$ m/s, and $c_{I_c} = 3750 \pm 50$ m/s, respectively. The differences among these values are small, and this is in agreement with the similar Debye level found in these three materials by inelastic neutron scattering experiments (INS) [10]. In both LDA and HDA the resonances become broader with increasing Q transfer. The determination of the absolute resonance widths, $\hbar\Gamma(Q)$, is complicated by two facts: (i) the values for $\Gamma(Q)$ are highly correlated with the background, and (ii), particularly in HDA, the features appearing with increasing Q on the low frequency side of the acousticlike peaks interfere with the fit. Because of these reasons we consider that a systematic dependence of $\Gamma(Q)$ on Q cannot be established although, as seen in Fig. 4, a description of $\Gamma(Q)$ by a quadratic function is possible on purely statistical grounds [14]. Independent of the exact Q dependence, the width of the resonances remains by far smaller than the excitation energy, $\hbar\Omega(Q)$, for all the considered Q values. This result is very different from the observation made so far

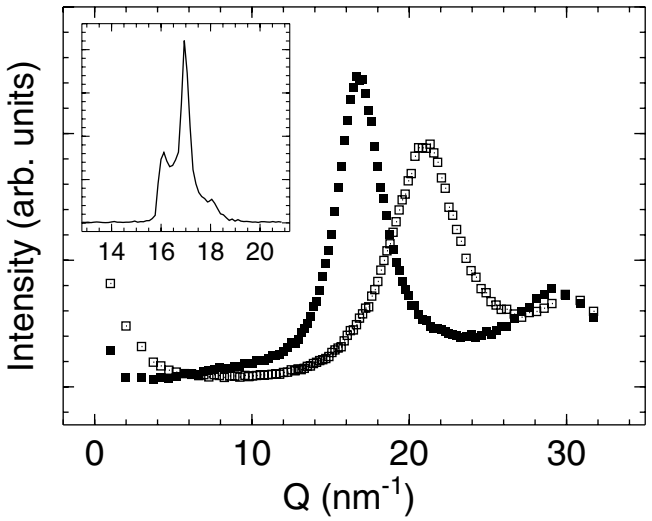

FIG. 1. Static structure factor of high-density (HDA) and low-density (LDA) amorphous ice as measured on the inelastic x-ray beam line prior to the inelastic experiments. No signs of Bragg peaks are observed, indicating that both amorphous phases are free of crystalline ice XII contaminations. The inset shows the diffraction pattern of cubic ice.

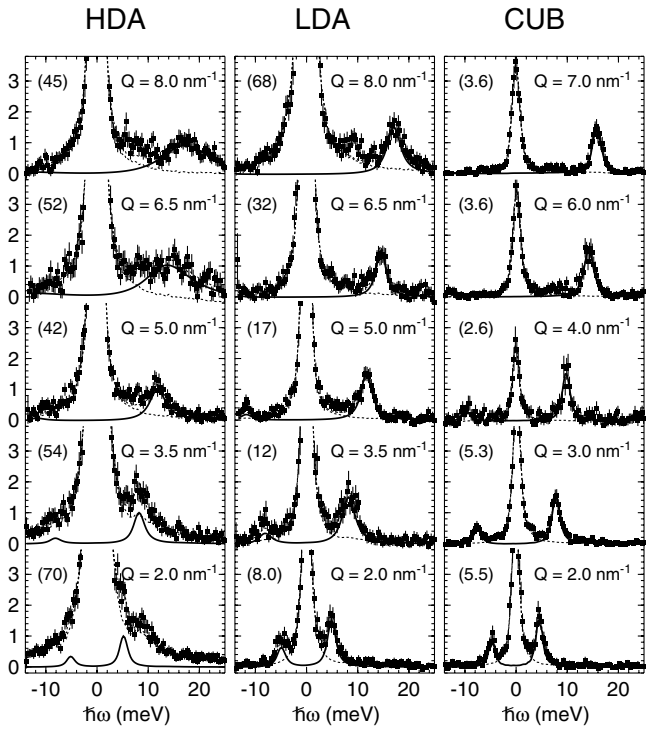

FIG. 2. Inelastic x-ray spectra of high-density amorphous (HDA), low-density amorphous (LDA), and crystalline cubic ice (CUB) at the indicated Q values lying mainly in the first pseudo-Brillouin zone. The dashed lines are fits to the signal using Lorenzian line shapes convoluted with the resolution function (equally indicated). The solid lines represent the inelastic contribution to the total fits. The numbers in brackets on the left of the elastic line give the elastic intensities in arbitrary units. Note the close resemblance of the sharp inelastic response of both amorphous phases to the crystalline phase.

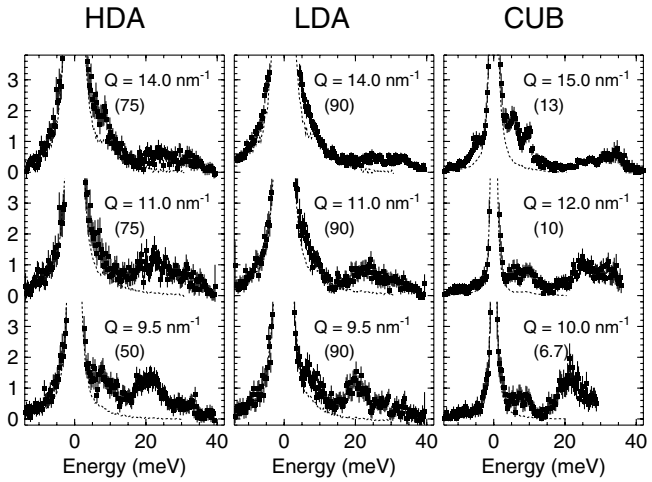

FIG. 3. Inelastic x-ray spectra of high-density amorphous (HDA), low-density amorphous (LDA), and crystalline cubic ice (CUB) at high Q values in the second pseudo-Brillouin zones. The dashed lines give the resolution functions. The elastic intensities are given in brackets. For these high Q values the excitations become part of a broad intensity distribution reminiscent of the density of states.

in other glassy systems. There, in fact, one observes an acoustic phononlike resonance with a quadratic dependence of $\Gamma(Q)$ on Q up to a value $Q = Q_m$ where the width $\Gamma(Q_m)$ starts to be comparable to the frequency $\Omega(Q_m)$. At Q larger than Q_m it is no longer possible to observe well-defined excitations.

Let us take the position, Q_M, of the first sharp diffraction peak as an indicator for the extent of structural correlations in the two amorphous phases. This allows us to define a pseudo-Brillouin zone [15] which extends to $Q_M/2 \approx 10$ nm^{-1} in HDA, and to $Q_M/2 \approx 8$ nm^{-1} in LDA. The quantity Q_m/Q_M has so far always been found smaller than 0.5 [6]. In the two amorphous ice phases studied here, excitations are very well defined up to Q-transfer

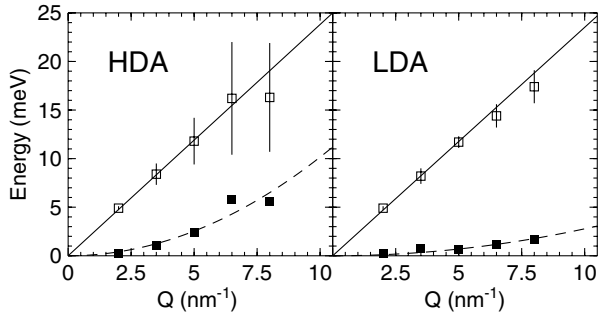

FIG. 4. Frequencies $\Omega(Q)$ (open symbols) and linewidths $\Gamma(Q)$ (full symbols and equally shown as vertical bars) as obtained by fitting Lorenzian functions to the inelastic x-ray spectra (fits shown in Fig. 2). The solid lines are linear fits to $\Omega(Q)$. Dashed lines are Q^2 fits to $\Gamma(Q)$. The good description of $\Gamma(Q)$ by a Q^2 function in the case of HDA should be taken with care, as the signal is definitely not Lorenzian-like for Q values larger than 5 nm^{-1} (see Fig. 2).

values approaching Q_M. In Ref. [6] the possible existence of a relation between the value of Q_m/Q_M and the degree of fragility of the considered glass [16] has been suggested. The high value of Q_m/Q_M, which seems to approach unity in these two glasses, would imply that amorphous ices, and especially LDA, are the extreme end of fragile glasses. This is in clear contradiction to the view that water passes through an inflection in the deeply supercooled region where the liquid behavior changes from extremely fragile to strong and ends up in the strong glassy state represented by LDA [17,18].

The observed similarity of LDA and ice I_c [19] holds equally for the excitations at $\approx$7 meV (Figs. 2 and 3), which appear at higher Q and recall the transverse dynamics found in ice I_h and liquid water [8]. In fact, as in these systems, the excitations set in around 5 nm^{-1} and become more pronounced beyond $Q_M/2$. In HDA the resemblance is less pronounced [20]. The translational part of the density of states for I_h, I_c, and LDA, as obtained from INS spectra [10], is peaked around 6.5 meV (D_2O). It is, therefore, to be expected that the IXS spectra show excitations in this energy region at low Q due to umklapp processes [21]. These processes take place via the Bragg peaks in the crystalline state and via the static structure factor in the case of LDA [22].

Despite the well-defined character of the low Q excitations in the two amorphous ice phases when compared to other glasses, one recovers a clear indication of the disordered character from the evolution of the inelastic spectrum at larger Q values. The spectra of LDA and HDA are less structured, lacking the sharp features observed in ice I_c.

To conclude, we reported on an IXS measurement of the $S(Q, E)$ of the two known phases of amorphous ice. This has allowed us to show that these two states of the water molecule possess a surprisingly crystal-like dynamic response. In both HDA and LDA the sound wave excitations are well defined. These experimental findings are in sharp contrast to the results found so far in other glasses and glass forming materials. In these systems, in fact, an important broadening has always been observed in the inelastic part of the dynamic structure factor $S(Q, E)$. In this Q region the scattering experiment becomes sensitive to the topological disorder which opens decay channels for sound excitations in addition to those available in the crystal. These channels are found practically absent in the case of the amorphous ice phases indicating a very low degree of local disorder. Structural results are controversially discussed and to date do not give a clear picture of the topology [23,24]. Experimentally only the pair correlation functions are directly accessible. Higher order correlations, among these the orientational correlation function, must be obtained in an indirect way [25], e.g., via the dynamic response. We deduce from our data highly intact hydrogen bond networks both in LDA and to some lesser degree equally in HDA. Although an intact network in itself is no warranty for the absence of decay channels—

e.g., an infinite random framework of corner-linked SiO_2 tetrahedra can undergo large phonon-assisted distortions [26]—it seems a necessary condition. In LDA this network is perfectly annealed as it is not obtained via a fast quench from the liquid. Because of the constraints of the network the number of states the system can sample on the ps time scale should be small, i.e., there is a small configurational entropy, a view which is compatible with molecular dynamics data [18]. HDA is expected to possess a larger configurational entropy, and on this basis one can justify that HDA has more "glassy behavior" than LDA.

Apart from structure and bonding the dynamical properties of the water molecule influence the decay of soundlike excitations both in crystalline and amorphous ice. We just want to point to the clear separation of translational and librational bands which independently of the structural details arises from the very small moment of inertia of the water molecule. This separation closes decay channels—e.g., present in SiO_2 [27]—involving resonances of acousticlike and librational modes, and may equally explain the absence of strong excess intensities in the inelastic neutron scattering data [10]. Temperature and the concomitant anharmonicities equally have to be given proper consideration in the discussion [27]. In the end only detailed molecular dynamics calculations on well-characterized ensembles combined with experiments on similar systems will be able to unambiguously give the reasons for the crystal-like dynamic response of amorphous ice phases.

We acknowledge A. Mermet for his help during the IXS measurements, B. Gorges and R. Verbeni for technical support, and F. Sciortino, C. A. Angell, and G. Ruocco for useful discussions. We also acknowledge the financial support of the Bundesministerium für Bildung und Forschung under Project No. 03FU4DOR5.

[1] P. H. Poole, T. Grande, C. A. Angell, and P. F. McMillan, Science **275**, 322 (1997).
[2] S. Harrington, R. Zhang, P. H. Poole, F. Sciortino, and H. E. Stanley, Phys. Rev. Lett. **78**, 2409 (1997).
[3] J. S. Tse, D. D. Klug, C. A. Tulk, I. Swainson, E. C. Svensson, C.-K. Loong, V. Shpakov, V. R. Belosludov, R. V. Belosludov, and Y. Kawazoe, Nature (London) **400**, 647 (1999).
[4] H. E. Fischer, F. J. Bermejo, G. J. Cuello, M. T. Fernández-Diaz, J. Dawidowski, M. A. González, H. Schober, and M. Jimenez-Ruiz, Phys. Rev. Lett. **82**, 1193 (1999).
[5] U. Balucani and M. Zoppi, *Dynamics of the Liquid State* (Clarendon Press, Oxford, 1994).
[6] F. Sette, M. H. Krisch, C. Masciovecchio, G. Ruocco, and G. Monaco, Science **280**, 1550 (1998).
[7] A. P. Sokolov, R. Calemczuk, B. Salce, A. Kisliuk, D. Quitmann, and E. Duval, Phys. Rev. Lett. **78**, 2405 (1997).
[8] G. Ruocco and F. Sette, J. Phys. Condens. Matter **11**, R259 (1999), and references therein.
[9] O. Mishima, L. D. Calvert, and E. Whalley, Nature (London) **310**, 393 (1984).
[10] H. Schober, M. Koza, A. Tölle, F. Fujara, C. A. Angell, and R. Böhmer, Physica (Amsterdam) **241B–243B**, 897 (1998).
[11] M.-C. Bellissent-Funel, J. Teixeira, and L. Bosio, J. Chem. Phys. **87**, 2231 (1987).
[12] M. Koza, H. Schober, A. Tölle, F. Fujara, and T. Hansen, Nature (London) **397**, 660 (1999).
[13] M. Koza, H. Schober, T. Hansen, A. Tölle, and F. Fujara, Phys. Rev. Lett. **84**, 4112 (2000).
[14] In any case care has to be taken in interpreting such broadening because the line shape of the resonances is unknown. For a single phonon it could be assumed a Lorenz function reflecting the finite lifetime of the excitation. However, when taking a powder average the line shape acquires a nonanalytic form even for the crystal due to the anisotropy within the multidimensional dispersion sheet.
[15] D. Caprion, P. Jund, and R. Jullien, Phys. Rev. Lett. **77**, 675 (1996).
[16] C. A. Angell, in *Relaxation in Complex Systems,* edited by K. L. Ngai and G. B. Wright (U.S. GPO, Washington, DC, 1984), p. 3.
[17] K. Ito, C. T. Moynihan, and C. A. Angell, Nature (London) **398**, 492 (1999).
[18] F. W. Starr, C. A. Angell, R. J. Speedy, and H. E. Stanley, arXiv.cond-mat/9903451.
[19] Cubic ice is not a perfect crystal due to the presence of staking faults [W. F. Kuhs, D. V. Bliss, and J. L. Finney, J. Phys. (Paris), Colloq. **48**, C1-631 (1987)]. This is an interesting subject in its own, however, without incidence on the discussion of the amorphous phases presented here.
[20] It should be pointed out that while ice I_c is a good reference system for LDA this may not be the case for HDA. HDA has supposedly a bonding topology closer related to high-density ice forms like ice XII, which is formed under similar conditions [12].
[21] Brute force fitting of a damped harmonic oscillator (DHO)—frequently used in previous analysis of IXS data—would lead to overdamping at large Q. The DHO, however, does not make any physical sense in the Q region where the spectra already reflect the specific features of the phonon density of states.
[22] U. Buchenau, Z. Phys. B **58**, 181 (1985).
[23] M.-C. Bellissent-Funel, Europhys. Lett. **42**, 161 (1998).
[24] L. Pusztai, Phys. Rev. B **61**, 28 (2000).
[25] A. K. Soper, J. Chem. Phys. **101**, 6888 (1994).
[26] K. Trachenko, M. T. Dove, K. D. Hammonds, M. J. Harris, and V. Heine, Phys. Rev. Lett. **81**, 3431 (1998).
[27] S. N. Taraskin and S. R. Elliott, Phys. Rev. B **59**, 8572 (1999).