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Thermal conductivity of amorphous ices

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The thermal conductivities κ of high-density amorphous (HDA) ice and low-density amorphous (LDA) ice were measured under pressure. The results for HDA show typical glasslike behavior, i.e., positive $d\kappa/dT$, whereas LDA exhibits *crystal-like* behavior, indicating that phonon-phonon scattering is dominant. LDA appears to be unique among apparently topologically disordered glasses to exhibit such behavior. Moreover, the results imply that LDA and glassy water formed by rapid cooling are different states.

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Amorphous solid water or amorphous ice can be formed by several routes such as condensation of water vapor onto a cold substrate (ASW), irradiation of ice Ih, and pressurization of ice Ih at temperatures below about 140 K. The latter was observed by Mishima and co-workers,[1] who also established that the product state, high-density amorphous (HDA) ice, transforms to a low-density amorphous (LDA) form at low pressures.[1] Their results and the present state of knowledge concerning amorphous ice and supercooled liquid water have been summarized in a review.[2] Both LDA and HDA show the typical x-ray diffraction halo patterns exhibited by amorphous states. Moreover, LDA exhibits a glass transition anomaly, whereas such has not yet been observed for HDA. Even if it is perhaps not fully established, both HDA and LDA will be referred to here as glassy states. In general, there is a liquid source phase associated with a glassy state, and structural data for water at 268 K (Ref. 3) show evidence for a continuous transformation from a low-density form to a high-density form of water upon isothermal pressurization. These have similar densities as LDA and HDA and the structure factors show considerable resemblance. In addition, results[4,5] show indirect evidence for a phase line between two liquid phases, which is the extension of that between HDA and LDA, and also that this phase line could end up in a critical point near 50 MPa, 230 K. These results support a hypothesis that LDA and HDA are identical with ASW formed at low and high pressures, respectively. Moreover, the existence of two liquid phases is one of several models that have been proposed to explain some of the unusual properties of water.

On the other hand, Johari[6] has discussed thoroughly the distinctions and interrelations between the amorphous states of water formed by the different routes. He concluded that the pressure produced LDA, as well as HDA, is most likely different from glassy states obtained by rapid cooling at 1 atm, which is supported by results of neutron scattering.[7,8] The number of the amorphous states of water and the expected liquid counterparts are therefore still disputed. It is not clear how the findings of distinct differences between high-pressure produced amorphous solid water, LDA and HDA, and that formed by rapid cooling (ASW) can be rationalized in the model of two liquid phases, which can be experimentally indirectly connected to HDA and LDA. It is obvious that much work in regard to these states still remains in order to elucidate some of the questions concerning the properties of water.

In this communication, we present results for the thermal conductivity κ of the high-pressure produced amorphous ices: HDA and LDA. One of the characteristics of topological glasses is the almost universal behavior of κ. This can be classified into three temperature regimes, where the highest is explored in this investigation. At low temperatures below a few K, κ varies as T^2, which can be explained in terms of two-level systems (TLS).[9] Above this regime, κ is constant, yielding a plateau, and subsequently increases further up to the glass transition temperature. The thermal conductivity in these two temperature regimes is less well understood but there are two models which have a potential to describe κ of glasses over a wide temperature range.

The soft potential model, which is a natural extension of the TLS model, can describe several characteristic properties of glasses. It provides a description for the behavior in κ (Refs. 10 and 11) and heat capacity, and can also account for the excess low-energy modes (boson peak) observed in, e.g., Raman spectroscopy. These are, in fact, fundamental for the description of κ since the plateau is accounted for by mainly resonance scattering of sound waves by soft localized vibrations—excess low-energy modes. The subsequent (second) rise in κ is attributed to weakening frequency dependence of their density of states.[11] As noted before,[12] some experimental results are not consistent with this model. For example, κ of amorphous silicon shows a plateau despite absence of a boson peak.

The other model attributes the plateau in κ to phonon localization.[13,14] Low-frequency phonons are delocalized and contribute to the heat conduction whereas those above a particular (localization) frequency are localized, or strongly localized in the model of Nakayama,[14] yielding the plateau in κ when the delocalized modes are fully excited as the temperature is raised. The second rise in κ is attributed to the onset of a new conduction mechanism: phonon assisted hopping of localized vibrations. The localized vibrations, associated with the boson peak, start to contribute to κ through a hopping mechanism mediated by phonons. Also in this case, there are results that contradict the model. For example, numerical calculations[15,16,12] show that the localization edge

is too far up in frequency to explain the plateau and the second rise of κ in terms of this model.

In addition to these and other models, there are many numerical calculations of κ for a disordered state.[15,16,12] The results show that the plateau occurs due to Rayleigh scattering, which yields a strong frequency-dependent decrease in the mean free path. As the mean free path decreases towards the order of the interatomic spacing, however, the frequency dependence becomes weaker, yielding a second rise in κ.

The behavior of κ for simple crystals, such as alkali halides, is distinctly different from that of glasses, and is well described within the Debye theory of crystals. At low temperatures, κ of pure crystals varies as T^3, following the behavior of the heat capacity. Further up in temperature, κ reaches a maximum when the dominant scattering mechanism changes from boundary scattering to three-phonon umklapp scattering. In the high-temperature region investigated in this work, near and above the Debye temperature, the theory predicts $\kappa \propto T^{-1}$, in fair agreement with most experimental observations. However, a particularly strong deviation from the T^{-1}, or ''ideal crystal-like'' behavior, has been observed for some inclusion compounds such as clathrate hydrates.[17] For these crystals, κ varies in the same manner as that for glasses, i.e., κ increases with temperature up to the fusion point. The most discussed model for this ''glasslike'' behavior is that localized vibrations, associated with the guest molecules, interact strongly with the heat-carrying vibrations.[18] A crystal can therefore exhibit glasslike κ, although it is unusual. However, to the best of our knowledge, there is no report of crystal-like behavior of κ for a glass. In this communication, we show that an apparently topologically disordered glass, LDA, exhibits such a feature.

The transient hot-wire method[19] was used to measure κ of H_2O, which had been purified using Milli-Q® Ultrapure Water Systems. H_2O was poured into a Teflon cell and mounted in a piston-cylinder type of apparatus of 45 mm internal diameter. The inaccuracy in κ is estimated to be $\pm 2\%$ at 100 K. The inaccuracy in temperature was estimated as ± 0.5 K and the inaccuracy in pressure as ± 40 MPa at 1 GPa and room temperature.

The HDA ice was formed by pressurizing ice Ih to about 1.3 GPa at 130 K (Fig. 1). The results for κ of ice Ih decreases with pressure, which is an unusual behavior that can be attributed to a decreasing shear modulus and therefore decreasing transverse sound velocity.[20] The amorphization process yields a fairly abrupt decrease of κ, which occurs at about 0.95 GPa. The transition Ih→HDA is completed at 1.1 GPa, where κ increases upon further pressurization, which is the normal behavior for a glassy state. Subsequently, the pressure was decreased at 130 K. At low pressure ($\sim$0.03 GPa), κ increased fairly suddenly and the pressure reading increased as an indication of a fast volume change associated with the HDA→LDA transition. The increase of κ at the HDA→LDA transition is somewhat surprising. The thermal conductivity of a phase generally increases with increasing density at constant temperature. Ice Ih and Ic are two of a few crystalline exceptions to this rule. Consequently, of two amorphous states of the same substance, it is most likely that the state with higher density should exhibit higher κ. This

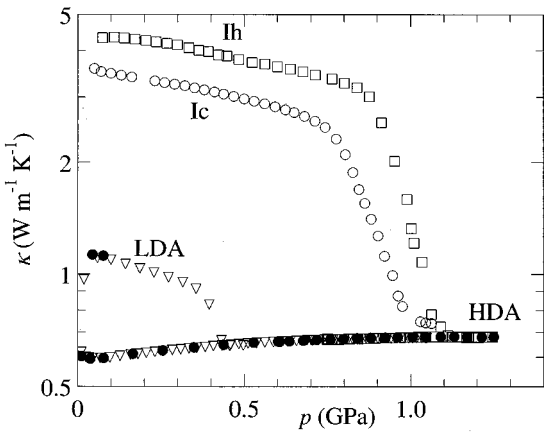

FIG. 1. Thermal conductivity as a function of pressure at 130 K. The HDA→LDA transition (0.03 GPa) is shown for two different runs, where one was stopped before the reverse transition, to study the isobaric temperature dependence of κ for LDA (see Fig. 2).

predicts a decrease of κ at the HDA→LDA transition, which is contrary to the findings here. (In a previous paper,[21] the increase of κ observed near 130 K was incorrectly interpreted as the LDA→Ic transition, and previously published data[21] therefore pertain to κ of HDA.) On the other hand, LDA exhibits smaller configurational entropy and therefore better order than HDA, which should favor an increase of κ.

Pressurization of LDA yielded a transition at 0.4 GPa at 130 K in fair agreement with the values 0.3 GPa for a temperature in the range 130–140 K (Ref. 22) and 0.5 GPa at 110 K.[23] An important observation is that κ decreases with pressure like that of Ih (Ic), though the pressure dependence is stronger in the former. A pressure-induced decrease in κ is very unusual for crystals and has not been observed previously for a glass. It is most likely that the reason for the decrease, associated with the decreasing transverse sound velocity, is closely connected to the change in structure and, therefore, this result provides indirect evidence for a structural similarity between LDA and Ih (Ic).

The result for $\kappa(T)$ of HDA is typical glasslike (Fig. 2), i.e., κ increases weakly with temperature up to the stability limit of HDA. HDA can transform either directly to Ic ($p = 0.07$ GPa) or via LDA ($p = 0.05$ GPa) as revealed by a wiggle in $\kappa(T)$. The data in the range 160–220 K pertain to a mixture of Ic and Ih. The latter has higher κ, yielding a weak temperature dependence of κ as Ic slowly transforms irreversibly to Ih. [Cooling of the sample from a temperature in this range yields crystal-like $\kappa(T)$.] As shown in Fig. 2, $\kappa(T)$ of LDA decreases with increasing temperature, which is unique for an apparently topologically disordered glass. The result is typical for a substance where umklapp scattering is important for limiting κ, which is in sharp contrast with results for other glasses. A fit shows that κ for LDA varies as $T^{-0.5}$ implying that umklapp scattering, which yields $\kappa \propto T^{-1}$, cannot solely account for phonon scattering in LDA. Results of HDA formed from LDA showed perfect agreement with those obtained before formation of LDA, certifying that our LDA ice contained no crystalline ice.

Since there are no measurements of κ for bulky ASW, it

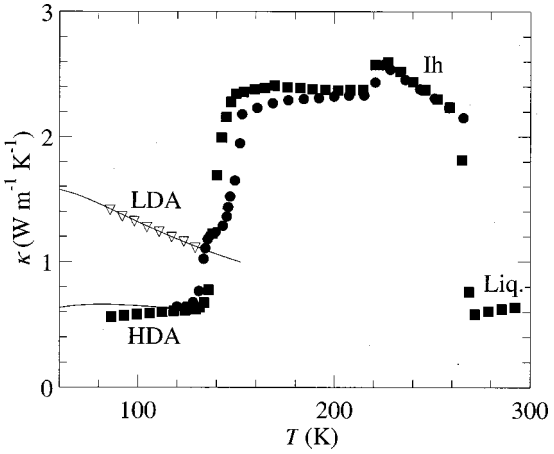

FIG. 2. Isobaric thermal conductivity as a function of temperature: (●) 0.05 GPa and (■) 0.07 GPa, and (▽) LDA at 0.1 GPa. Lines represent a fit (LDA) and a calculation (HDA) as explained in the text.

cannot be compared directly with our results for LDA. However, κ does not normally change much at the glass transition temperature T_g, and we can thus make a comparison with that expected by using the results for liquid water. Literature data for κ of supercooled liquid water (obtained from salt solutions), decrease linearly with decreasing temperature down to 230 K, which agrees with the behavior observed here in a more narrow temperature range. It is most likely that κ should continue to decrease roughly linearly down to T_g, or at least not increase. A fairly common behavior at T_g is that $d\kappa/dT$ changes, which can be attributed to the change in the coefficient of thermal expansion, but that there is no large discontinuous change in κ as at a phase transition. The glass transition for LDA occurs at about 129 K,[6] but cannot be identified in the data for κ. A linear extrapolation of the data for liquid water down to 129 K shows that κ for LDA must decrease discontinuously at T_g to connect to those of supercooled water, which is an implausible behavior. Consequently, the data in Fig. 2 support previous findings of distinct differences between ASW and LDA (Ref. 6) and indicate that LDA does not transform to normal supercooled liquid water on heating. If we do the same comparison between HDA and liquid water then this distinction is less apparent, as seen in Fig. 2, and might be accounted for by the difference in density. Considering only results for κ, HDA could be a high-pressure amorphous solid state of liquid water, i.e., a hypothetical ASW formed by rapid cooling at 1 GPa.

The unique crystal-like κ for LDA has support in results of the vibrational spectrum and structure for LDA, which show close similarities with those of Ic and Ih.[7,8,24] Moreover, inelastic x-ray scattering (IXS) shows that crystal-like excitations are observed at higher frequencies in LDA than in HDA,[25] which favor a larger κ for LDA. In addition, HDA exhibits excess low-energy excitations,[26–28] whereas such cannot be observed or are present to a much smaller extent in LDA. This latter result might be associated with the observation of high-frequency propagating modes since low-energy excitations may arise as a result of strong scattering or perhaps interact strongly with propagating modes. The widths Γ of excitations that are observed in IXS (Ref. 25) are, in comparison with most other disordered states, unusually narrow for momentum transfers Q up to as large as 5 nm^{-1} and 8 nm^{-1} for HDA and LDA, respectively. This indicates that the phonon lifetime is relatively long or, equivalently, that the scattering is relatively weak, in particular in LDA. Since the dispersion relation stays approximately linear in this range and Γ varies quadratic with Q, the scattering rate should vary quadratic with frequency Ω. At the end of the studied momentum range, the dispersion bends and the scattering rate appears to change towards stronger frequency dependence. When Ω becomes independent of Q, and Γ approaches the size of Ω, the excitations change its nature from propagation towards localization. Due to stronger scattering this should occur at lower Ω for HDA than for LDA, indicated by the results of IXS. These results are qualitatively consistent with the results for κ but we can also investigate if the change in κ at the LDA→HDA transition can be explained quantitatively by the stronger scattering in HDA, implied by a roughly 3.5 times broader $\Gamma(Q)$. In order to do this we used the relaxation time method for κ together with the Debye model.[29,30] We assume a simple form for the relaxation time, consisting of two parts, to roughly account for phonon-phonon scattering and phonon scattering associated with the topological disorder. For the former, we used an expression for the relaxation time of umklapp scattering, previously applied in an investigation of κ for Ih.[30] To account for scattering associated with the topological disorder, it is reasonable to use an inverse relaxation time proportional to Ω^2 in analogy with the results of IXS up to fairly high frequencies.

The result using this model for LDA, with the scattering strengths as adjustable parameters and the other parameters taken the same as those for Ih, is shown in Fig. 2. The result for the scattering strength of umklapp scattering is of the same order (about three times larger) as that found for Ih. The scattering strength associated with the topological disorder is of the same order as that estimated from the IXS peak width, assuming that the width is determined entirely by this scattering. Subsequently, the result for HDA was calculated by increasing the scattering strength associated with the topological disorder by a factor 3.5, in correspondence with the 3.5 times broader Γ. The umklapp scattering strength was kept the same as that for LDA, i.e., no free parameters were used to calculate κ for HDA. As shown in Fig. 2, the model accounts roughly for both the changes in magnitude and temperature dependence of κ. This type of calculation cannot be given too much weight considering the large uncertainties in the model and that IXS probes longitudinal modes, but it implies a quantitative agreement between IXS data and the results for κ. A fit using a more elaborate model that accounts also for point defect scattering indicates that this scattering is insignificant. However, due to the crudeness of the relaxation time model and limited data, it is not impossible that point defects and other scattering centers, which are not described by the relaxation time in our simple model, give a contribution to the thermal resistivity.

Both the soft potential model and the model of phonon assisted hopping can account qualitatively for κ of LDA. The former ascribes glasslike behavior of κ to strong phonon scattering by localized low-energy excitations and, consequently, the absence of these could lead to crystal-like behavior. At the LDA→HDA transition, the decrease of κ is accounted for by the additional phonon scattering from emerging low-energy modes. The model of phonon assisted hopping ascribes glasslike behavior to phonon localization, where some of the localized states, strongly localized modes, are associated with the boson peak. The absence of the latter would signal the absence of phonon localization and, therefore, possible crystal-like behavior of κ. However, it is difficult to explain the results for HDA since IXS does not show phonon localization within the investigated momentum range.

The results reported here show strikingly different behavior of $\kappa(T)$ for two apparently topological glasses, HDA and LDA. HDA exhibits typical glasslike behavior whereas LDA shows crystal-like κ. The relaxation time model for κ together with IXS results for relaxation times can account for these results. IXS shows that the scattering strength due to disorder is about 3.5 times larger in HDA than in LDA. This larger scattering strength correlates with emerging low-frequency excess modes, which could therefore be at least partly responsible for the stronger scattering in HDA. Previous results for κ of amorphous silicon[12] show, however, that glasslike behavior is not necessarily associated with excess vibrations so these cannot be the origin of strong scattering in all glasses. It is therefore possible that these modes often arise under strong scattering conditions instead of being its origin. A low-temperature investigation of κ for LDA and HDA would certainly be interesting, revealing a possible plateau and T^2 dependence, but this is hampered by experimental difficulties.

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