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Unusual Grüneisen and Bridgman parameters of low-density amorphous ice and their implications on pressure induced amorphization

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The low-temperature limiting value of the Grüneisen parameter for low-frequency phonons and the density dependence of the thermal conductivity (Bridgman parameter) of low-density amorphous (LDA) ice, high-density amorphous (HDA) ice, hexagonal ice Ih, and cubic ice Ic were calculated from high-pressure sound velocity and thermal conductivity measurements, yielding negative values for all states except HDA ice. LDA ice is the first amorphous state to exhibit a negative Bridgman parameter, and negative Grüneisen parameters are relatively unusual. Since Ih, Ic, and LDA ice all transform to HDA upon pressurization at low temperatures and share the unusual feature of negative Grüneisen parameters, this seems to be a prerequisite for pressure induced amorphization. We estimate that the Grüneisen parameter increases at the ice Ih to XI transition, and may become positive in ice XI, which indicates that proton-ordered ice XI does not amorphize like ice Ih on pressurization. © 2005 American Institute of Physics. [DOI: 10.1063/1.1869352]

I. INTRODUCTION

Hexagonal and cubic ices form an amorphous state, known as high-density amorphous (HDA) ice, upon isothermal pressurization at 77 K to above 1.2 GPa,¹ which is most likely due to a pressure induced mechanical instability of the ice lattice.² The HDA state transforms further to a low-density amorphous (LDA) state on heating at atmospheric pressure up to ~ 125 K. Although the glass transition of bulk HDA has not been observed, the state exhibits typical behavior for glasses such as amorphous x-ray pattern,¹ low-energy excitations,^{3–5} and glasslike heat transport properties.⁶ In contrast, LDA exhibits striking crystallinelike features despite displaying both an amorphous x-ray pattern¹ and a weak glass transition signature at 124 K in data for heat capacity data using slow heating rate.⁷ Moreover, inelastic x-ray scattering shows that phononlike excitations are present in LDA up to unusually high frequencies.⁸ Furthermore, data for thermal conductivity κ of LDA show strongly decreasing values at increasing temperatures. In fact, κ varies as $T^{-0.6}$, which is the same as that for crystalline ices V and VI, and far from the expected $\kappa(T)$ of amorphous states and that shown by HDA ice, which is a weakly increasing κ with increasing temperature. The strongly decreasing κ is likely due to relatively strong phonon-phonon scattering, which seems inconsistent with an amorphous state, but this is apparently the case in LDA ice. Moreover, low-energy excitations are absent, or present in much smaller extent, in LDA than in HDA.^{4,5} It is evident that LDA ice is a state of fundamental interest and that it is desirable to gain further knowledge about its properties. In this work, we use data for the pressure dependence of the thermal conductivity and the sound velocity to calculate the Bridgman parameter g and the low-temperature limiting Grüneisen parameter. The former is

defined by $g = (\partial \ln \kappa / \partial \ln \rho)_T$, where ρ is the density, i.e., $g = B_T \times (\partial \ln \kappa / \partial p)_T$, where B_T is the isothermal bulk modulus. The mode Grüneisen parameter γ_i is given by $\gamma_i = (\partial \ln \nu_i / \partial \ln \rho)_T$, where ν_i is the phonon frequency of mode i . As shown here, the low-temperature limiting value of an average for the Grüneisen parameters of LDA ice is negative, which implies a negative thermal expansion coefficient at low temperatures. Moreover, an estimate for the change of the Grüneisen parameter at the ice Ih to ice XI transition shows that it increases and may become positive in ice XI, indicating that this phase would not amorphize, or amorphize at a significantly higher pressure than ice Ih. A higher amorphization pressure for ice XI (~ 3.5 GPa) than that for ice Ih (~ 1 GPa) has recently been reported in an investigation using computer simulations.⁹

II. RESULTS AND DISCUSSION

To calculate the Bridgman parameter of LDA, we have used data for $\kappa(p)$ at 130 K (Ref. 6) together with data for $\rho(p)$ measured in the range 130–140 K.¹⁰ The isothermal bulk modulus B_T calculated from these data (8.2 GPa) agree well with the adiabatic bulk modulus B_S measured by Gromnitskaya *et al.*¹¹ on heating at 0.05 GPa (~ 8.1 GPa at 140 K), but is smaller than that calculated from isothermal data for density at 110 K (Ref. 11) (~ 11 GPa). [Data for $\rho(p)$ of LDA at 77 K (Ref. 10) give $B_T \sim 11$ GPa as an average in the range 0.1–0.5 GPa, and a significantly smaller value near 1 atm.] An equation that relates the two bulk moduli to each other: $B_S = B_T(1 + \beta \gamma_{TH} T)$, where β is the volume thermal expansion coefficient and γ_{TH} is the thermodynamic Grüneisen parameter,¹² shows that the difference between B_S and B_T is about 0.5% for ice Ih at these temperatures, and the difference for the other states of ice should not be very much

FIG. 1. (a) Logarithm of the thermal conductivity of low-density amorphous ice plotted against logarithm of density. (b) Logarithm of the thermal conductivity of high-density amorphous ice plotted against logarithm of density. The density values correspond approximately to the pressure range 0.05–0.35 GPa.

larger. The results for $\kappa(\rho)$ of LDA ice using $B_T=8.2$ GPa are shown in Fig. 1(a), and yield $g=-5.2$. Generally, amorphous states exhibit values close to 3, where liquid water is a slight exception having $g=2$ at 303 K,¹³ but a negative value has not been found before. The results for $\kappa(\rho)$ of HDA, shown in Fig. 1(b), yield $g=1.7$ at 130 K. This value was calculated using $B_T=8.5$ GPa. The data of Mishima,¹⁰ in the range 130–140 K, yield $B_T=8.2$ GPa, whereas data of Gromnitskaya *et al.*¹¹ show $B_s=8.8$ GPa at 130 K and 0.05 GPa. The value for g of HDA is somewhat low in comparison with other amorphous states, but about the same size as that for liquid water at 303 K. However, since g for amorphous states might vary slightly with temperature, and the temperature dependencies for g of HDA and liquid water are not known, it is not possible to conclude that these states have the same values for g under the same p , T conditions. It should be noted that the value used here for the calculation of g corresponds roughly to the pressure range of the $\kappa(p)$ values (0.05–0.35 GPa). At high pressures, B_T increases significantly. However, this also affects the data for $\kappa(p)$, which increases less strongly with pressure and, consequently, the calculated value of g in this higher pressure range would not be much different. All data used for the calculations as well as the results are summarized in Table I.

Results for hexagonal ice Ih and cubic ice Ic are shown in Figs. 2(a) and 2(b), respectively. For ice Ih, the results yield $g=-4.4$ at 130 K using $B_T=10.0$ GPa. Slack¹⁴ estimated $B_T=10.6$ GPa at 120 K, Johari's measurements¹⁵ at 77

TABLE I. Values used for calculation of the Bridgman parameter g .

State	B_T (GPa)	$(\partial \ln \kappa / \partial p)$ (GPa ⁻¹)	T (K)	P (GPa)	g
LDA	8.2	-0.63	130	0.05–0.35	-5.2
HDA	8.5	0.20	130	0.05–0.35	1.7
Ih	10.0	-0.44	130	0.15–0.55	-4.4
Ic	10.5	-0.34	130	0.15–0.55	-3.6
Ih	10.0	-0.45	58	0.1–0.16	-4.5
XI	10.0	0.26 ^a	58	0.1–0.16	2.6

^aAn estimation of the value for a 100% pure sample of ice XI.

K yielded $B_T=10.0$ GPa while Gromnitskaya *et al.*¹¹ found $B_s=9.5$ GPa near atmospheric pressure at 77 K. Mishima's data¹⁰ for ice Ic at 145 K yield $B=10.5$ GPa, and this value was used to calculate $g=-3.6$ for ice Ic.

In order to calculate the low-temperature limiting value for Grüneisen parameter γ we have used a similar approach as Slack,¹⁴ which was based on a theory by Sheard.¹⁶ For each mode

$$\gamma_i = 1/3 + B_T(\partial \ln \nu_i / \partial p)_T, \quad (1)$$

where ν_i is the sound velocity of mode i . The mode values were calculated using data for the transverse velocity $\nu_T(p)$ and longitudinal velocity $\nu_L(p)$ averaged over all directions, and the total γ was obtained by weighting the γ_L and γ_T values according to the mode contribution to the low-temperature heat capacity, $\gamma_{tot}=(\theta_L^{-3}\gamma_L+2\theta_T^{-3}\gamma_T)/(\theta_L^{-3}+2\theta_T^{-3})$. Slack¹⁴ estimated a transverse and longitudinal

FIG. 2. (a) Logarithm of the thermal conductivity of hexagonal ice plotted against the logarithm of density. (b) Logarithm of the thermal conductivity of cubic ice plotted against the logarithm of density. The density values correspond approximately to the pressure range 0.15–0.55 GPa.

TABLE II. Values used for calculation of the Grüneisen parameter.

State	B_T (GPa)	$(\partial \ln \nu_T / \partial p)$ (GPa ⁻¹)	$(\partial \ln \nu_L / \partial p)$ (GPa ⁻¹)	T (K)	ν_T (m s ⁻¹)	ν_L (m s ⁻¹)	γ_T	γ_L	γ_{tot}
LDA	11.0	-0.111	-0.030	110	2000	4090	-0.89	0	-0.84
HDA	10.0	0.112	0.192	77	2070	3770	1.45	2.25	1.51
Ih	10.0	-0.116	0.142	77	2070	3970	-0.82	1.75	-0.65
Ic				130			-0.65 ^a		-0.65 ^a
XI				58			0.59 ^a		0.59 ^a

^aValues calculated from Eq. (4) using data for g given in Table I.

Debye temperature based on data for the phonon energies at the Brillouin-zone boundaries whereas we have instead used ν_T and ν_L for the weighting factor in accordance with the Debye relation, $\theta_D \propto \nu$, i.e.,

$$\gamma_{tot} = (\nu_L^{-3} \gamma_L + 2\nu_T^{-3} \gamma_T) / (\nu_L^{-3} + 2\nu_T^{-3}). \quad (2)$$

All data for the sound velocities, densities, bulk, and shear moduli were taken from the Figs. 4 and 6 of Gromnitskaya *et al.*,¹¹ except for B_T of ice Ih, which seems slightly low ($B_S = 9.5$ GPa) at 77 K. We have instead used the value estimated here, which is based on a number of previous measurements^{11,14,15} ($B_T = 10$ GPa). All the values used for the calculations are summarized in Table II.

For LDA ice, we find $\gamma_T = -0.89$ and $\gamma_L = 0$ from Eq. (1), which yield $\gamma_{tot} = -0.84$, using $\nu_T = 2000$ m s⁻¹ and $\nu_L = 4090$ m s⁻¹ in Eq. (2). The value for B_T of LDA at 110 K, calculated from data for density in the range 0–0.4 GPa,¹¹ appears somewhat large ($B_T = 11$ GPa). Moreover, the value for γ_L is uncertain due to lack of data for $\nu_L(p)$ of LDA. The values for $\nu_L(p)$ were calculated from the relation $\nu_L^2 = \rho^{-1}(B_S + G \times 4/3)$, where B_S was obtained from $\rho(p)$. However, even if γ_L is significantly larger than that calculated here, this would not change γ_{tot} much since the weight of the value is low. (Using $\gamma_L = 1$ yields $\gamma_{tot} = -0.78$.) Although, the values for γ of LDA ice are uncertain, γ_{tot} and γ_T are certainly negative and of about the same size as those for ice Ih (see below). The result for HDA ice is $\gamma_{tot} = 1.51$ ($\gamma_T = 1.45$, $\gamma_L = 2.25$, $\nu_T = 2070$ m s⁻¹ and $\nu_L = 3770$ m s⁻¹).

The results for ice Ih at 77 K are $\gamma_T = -0.82$ and $\gamma_L = 1.75$, which yield a weighted $\gamma_{tot} = -0.65$ using $\nu_T = 2070$ m s⁻¹ and $\nu_L = 3970$ m s⁻¹. This value agrees reasonably well with that calculated using the definition of the thermodynamic Grüneisen parameter,

$$\gamma_{TH} = \frac{\beta B_S V}{C_p}, \quad (3)$$

where V is the volume and C_p is the heat capacity, which is $\gamma_{TH} = -0.3$ at 50 K (Ref. 12) and $\gamma_{TH} \sim -0.8$ at 0 K using a linear extrapolation. In their calculation of γ_{TH} , Röttger *et al.*¹² used their own data for V and β ,¹² and data for B_S and C_p of Dantl¹⁷ and Giaque and Stout,¹⁸ respectively. Our value for γ_{tot} of ice Ih is slightly larger than the value calculated by Slack¹⁴ (-0.78) and the difference is due to the use of different weighting factors and the larger value found here for γ_L .

There are no sound velocity data available for calculation of γ_{tot} of ice Ic. However, it is possible to make a rough estimate of γ_{tot} based on the density dependence of κ . Theory for κ of crystals yields¹³

$$g = 3\gamma + 2q - 1/3, \quad (4)$$

where $q = -(\partial \ln \gamma / \partial \ln \rho)_T$. An estimate made by Slack¹⁴ shows $q \sim \gamma$ for ice Ih, which makes it possible to separate the contributions of the transverse and longitudinal modes to κ by calculations of g_L and g_T from Eq. (4) and using $g_{tot} = g_L(\kappa_L / \kappa_{tot}) + g_T(\kappa_T / \kappa_{tot})$. Slack¹⁴ calculated that almost 100% (93%) of the heat was carried by the transverse phonons at 120 K. The same calculation done here using Eq. (4) gives that 97% is carried by the transverse modes in ice Ih near 130 K. Using the rough result that 100% of the heat is carried by the transverse phonons at 130 K, yields $\gamma_{tot} \sim \gamma_T \sim (g + 1/3)/5$, i.e., $\gamma_{tot} \sim \gamma_T \sim -0.65$ for ice Ic ($g = -3.6$). This is an underestimate of γ_{tot} since some of the heat is definitely carried by the longitudinal modes, but it shows that γ_{tot} and γ_T of ice Ic are certainly negative and of about the same size as those of ice Ih. Moreover, this is probably an overestimate for γ_T since γ_L of ice Ic should be positive, i.e. γ_T of ice Ic is likely smaller than -0.65 . In fact, γ_T of Ic should probably be slightly more negative than that of ice Ih. Experimentally it is found that Ic amorphizes at a lower pressure than ice Ih. The amorphization of Ic occurs at a (nominal) pressure of 0.99 GPa, whereas that of ice Ih occurs at 1.07 GPa in dilatometry measurements at 77 K.¹⁹ At 130 K data for κ (Ref. 6) show an onset of amorphization at a pressure of ~ 0.7 and 0.78 GPa for ice Ic and Ih, respectively. The results obtained here show that γ_T as well as γ_{tot} are negative for all states that exhibits amorphization or transformation into the HDA state. Consequently, the negative Grüneisen parameters of ice Ih and Ic (as well as LDA) imply the possibility of pressure induced amorphization. Moreover, the implications of negative values are softening of modes, and a more negative value for γ_T corresponds to a stronger degree of softening. (This result for ice Ic implies that if transformations to other crystalline forms could be avoided, ice Ic would melt upon pressurization at high temperatures.) It is therefore likely that the slightly lower amorphization pressure of ice Ic than ice Ih should be reflected in a more negative value for γ_T . This should lead a more pronounced degree of mode softening upon pressurization and therefore a lower pressure for the onset of amorphization. Such an inference would agree with the finding here that LDA ice has a negative and lower value for γ_T and, in par-

ticular, γ_{tot} than ice Ih although the difference in γ_T is probably within the inaccuracy of the calculations. Data for κ (Ref. 6) show a significantly lower transformation pressure of LDA in comparison with the amorphization pressure of ice Ih. The LDA to HDA transformation at 130 K starts at 0.36 GPa, which is more than 0.4 GPa below the onset of ice Ih amorphization. Even though the values for γ_T and γ_{tot} provide a measure of the affinity for transformation or amorphization into HDA, the picture seems too simple for a detailed analysis considering the small difference in γ_T , at least in the case of comparing the amorphous LDA state with the crystalline phases.

As discussed above, the Grüneisen parameters of both ices Ih and Ic, as well as LDA ice are negative. Negative Grüneisen parameters are rather unusual but occur here for three states that all display pressure induced instability and collapses to an amorphous state HDA ice, which exhibit a positive value. Consequently, negative γ , or rather negative γ_T , seems to be a prerequisite for amorphization or transformation to HDA ice upon pressurization. This result can be used to discuss qualitatively the issue whether or not the proton ordered phase of ice Ih, i.e., ice XI, would amorphize upon pressurization. A recent simulation⁹ indicates that the lattice would become unstable at ~ 3.5 GPa upon pressurization. As found here, the Grüneisen parameter of the transverse modes should be negative for this to occur. Since data for $\kappa(p)$ are available at low temperatures, we can estimate the value for γ_T , using the same procedure as done above for ice Ic, and which was based on results for ice Ih. The approximation that the heat is mainly carried by the transverse modes should be even better for ice XI, since the data for $\kappa(p)$ were obtained at lower temperatures.

In order to obtain ice XI, one must use a dopant to relax the constraints imposed by the ice rules. Tajima *et al.*^{20,21} have showed that small amount of the dopant KOH induces the proton ordering transition below about 72 K. However, the transition is still sluggish and only about 68% of the sample transforms even if it is annealed for several days below 72 K. Consequently, a measurement of $\kappa(p)$ for such a sample shows the result for a mixture of about 68% ice XI and 32% ice Ih.

Andersson and Suga,²² have measured $\kappa(p)$ for the mixture of $\sim 68\%$ ice XI and $\sim 32\%$ Ih as well as for ice Ih at 58 K. The results for ice Ih at 58 K for the range 0.1–0.16 GPa yield $g = -4.5$ using $B_T = 10.0$ GPa. The results for ice XI, yield $g = 0.3$ assuming the same value for B_T as that of ice Ih. The values are somewhat uncertain due to the limited pressure range as well as the uncertainty in B_T , which is taken from the estimate at higher temperatures. However, the results show that g increases significantly at the proton ordering transition (see Fig. 3), despite that only 68% of the Ih transforms. Assuming that the value for g changes linearly with the amount of sample transformed, we can estimate g for pure ice XI, yielding $g = 2.6$. Using Eq. (4), and the assumptions described above, this value can be used to calculate an approximate value for γ_T , which according to this estimate should be positive. Using the same assumptions as for ice Ic, i.e., that almost 100% of the heat is carried by the

FIG. 3. Logarithm of the thermal conductivity for ice Ih (open symbols) and a mixture of ice XI ($\sim 68\%$) and ice Ih ($\sim 32\%$) (filled symbols) plotted against pressure. The values have been normalized with the value for κ at 0.1 GPa.

transverse modes and that $\gamma \sim q$, yields $\gamma_T = 0.59$ for ice XI. The results indicate that γ_T increases at the Ih to XI transition and even becomes positive.

The sign of the thermodynamic Grüneisen parameter can also be derived using data for volume expansion. Equation (3) shows that γ_{TH} will have the same sign as the thermal expansion, i.e., it will also be negative if ice XI behaves like ice Ih and has a negative thermal expansion at low temperatures. The volume as a function of temperature can be obtained from neutron diffraction experiments, but the inevitable mixture of Ih and XI in the sample affects the results making the determination uncertain. The structure of D_2O ice XI was determined by Leadbetter *et al.*,²³ and the lattice parameters have later been refined by Line and Whitworth,²⁴ who used an improved procedure for obtaining ice XI and could therefore obtain larger amount of ice XI. Despite this, the results for D_2O XI were apparently affected by strains caused by untransformed D_2O Ih. Using data for the lattice parameters in the range 5–70 K for D_2O XI (Ref. 24) yields $\beta = -2(5) \times 10^{-6} \text{ K}^{-1}$. A calculation for D_2O Ih, using data at identical temperatures as for D_2O XI,² yields $\beta = -12(1) \times 10^{-6} \text{ K}^{-1}$ as an average in the temperature interval. Consequently, the result is inconclusive whether or not the thermal expansion of ice XI is positive due to the large standard error in β for D_2O ice XI, but the data show the same trend as the data for κ , i.e., that γ increases and may become positive in ice XI.

In the above discussion, we have not used “amorphization” to describe the LDA to HDA transformation. However, from the results of the thermal conductivity measurements⁶ as well as inelastic x-ray scattering,⁸ it is obvious that there must be a higher degree of order in LDA than HDA ice, which has also been inferred on the basis entropy calculations.²⁵ Consequently, even if both states apparently exhibit typical amorphous halo x-ray pattern, the order existing in LDA ice, and which is capable of providing a path for phononlike excitations, must be destroyed during the transformation. In that sense, the LDA to HDA transformation is also an amorphization process.

III. SUMMARY

As shown here, the values for the Bridgman and Grüneisen parameters of low-density ice, where the latter is the limiting low-temperature value, are both negative. No amorphous state has previously exhibited negative density dependence for the thermal conductivity, i.e., negative Bridgman parameter. It is also unusual that crystalline phases exhibit negative values, but both hexagonal and cubic ice show negative values, which suggests a structural similarity between these states, which has also been concluded before.^{26,6} The negative values for the transverse Grüneisen parameters of all these three states show that this is apparently a prerequisite for amorphization or transformation to the high-density amorphous state upon pressurization. Thus, the calculation here that pure ice XI may have a positive value indicates that this phase does not amorphize upon pressurization, or amorphizes at significantly higher pressure than ice Ih. Moreover, the negative values for the total low-temperature limiting Grüneisen parameter of hexagonal, cubic, and low-density amorphous ice show that these states should have negative thermal expansion coefficients at low temperature, whereas that of pure ice XI may be positive.

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