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Influence of isotopic disorder on solid state amorphization and polyamorphism in solid H_2O-D_2O solutions

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We present a low-temperature and high-pressure ultrasonic study of elastic properties of isotopic H_2O-D_2O solid solutions, comparing their properties with those of the isotopically pure H_2O and D_2O ices. Measurements were carried out for solid state amorphization (SSA) from 1h to high-density amorphous (HDA) ice upon compression up to 1.8 GPa at 77 K and for the temperature-induced (77−190 K) u-HDA (unrelaxed HDA) → e-HDA (expanded HDA) → low-density amorphous (LDA) → 1c cascade of ice transformations near room pressure. There are many similarities in the elasticity behaviour of H_2O, D_2O, and H_2O-D_2O solid solutions, including the softening of the shear elastic modulus as a precursor of SSA and the HDA → LDA transition. We have found significant isotopic effects during H/D substitution, including elastic softening of H_2O-D_2O solid solutions with respect to the isotopically pure ices in the case of the bulk moduli of ices 1c and 1h and for both bulk and shear elastic moduli of HDA ice at high pressures (>1 GPa). This softening is related to the configurational isotopic disorder in the solid solutions. At low pressures, the isotope concentration dependence of the elastic moduli of u-HDA ice changes remarkably and becomes monotonic with pronounced change of the bulk modulus (≈20%).

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I. INTRODUCTION

Water is a key substance for the development of life and all global bio- and geochemical cycles on the earth**.** However, the interest in water research is associated not only with its planetary role [1] and importance for the astrophysics of the solar system [1,2] but also with one of the most complicated solid state phase diagrams of water under pressure [3–5] and a variety of its puzzling anomalies [4–7]. As many as 16 crystalline modifications of ice are currently known [4,5] along with at least three different amorphous phases obtained by varying pressure and temperature [4–8]. The discovery of such phenomena as solid state amorphization (SSA) of 1h hexagonal ice [9] and polyamorphism (transition between amorphous phases) [10,11] for water gave an impetus to the development of the new research area in high-pressure condensed matter physics (see also [4–8,12–17] and references therein). The transformation of unrelaxed to expanded high-density (u-HDA → e-HDA) ice was discovered and studied in detail in Ref. [12]. Our ultrasonic study of SSA and polyamorphism in ice demonstrated the softening of the shear elastic modulus as a precursor of SSA and the u-HDA → e-HDA and the e-HDA → LDA (low-density amorphous) ice transitions [18–21].

At the same time, ice phases are of great interest as an experimental object for the study of isotopic substitution effects. The substitution of hydrogen by deuterium in the ice should lead to the one of the most significant changes in the mode oscillation frequencies related to libration and intramolecular [O-H(D) stretching and H(D)-O-H(D) bending modes] vibrations in water. In the classical harmonic limit, their relationship is close to $\sqrt{2}$, determined by the D/H mass ratio (a higher-frequency ratio for intramolecular modes could occur for hydrogen substitution by tritium). Indeed, infrared absorption [22–25] and Raman spectroscopy [26–29], as well as inelastic neutron scattering [30–33], confirm a ∼40% shift of the corresponding frequencies for the different aggregate states of water and its different solid phases. In this case, the shift in intermolecular vibrations is about 3%−7% [22–33] (in the classical limit, the frequency ratio is equal to $\sqrt{18/16} \approx 1.06$), and it is also relatively large for isotopic H/D substitution due to the small mass of H_2O molecules. Since hydrogen and deuterium are the lightest atoms, quantum effects, such as multiparticle quantum correlation effects [34–36] and additional quantum delocalization and tunneling along O–H $\cdots$ O bonds of protons [36–41] can significantly influence the isotopic differences between properties of ice and water. Both experimental studies and quantum simulations reveal the importance of quantum effects for H/D substitution in water [38–43] and amorphous ices [37,44].

Nevertheless, the isotopic analogs of ice and water have quite similar thermodynamic properties [3–5], since the isotopic contribution to thermodynamic properties is usually insignificant because it comes from quantum effects (zero oscillation energy). For example, the boiling and melting temperatures of H_2O are only 0.3% and 1.3% higher, respectively, than those of D_2O [4,5]. The pressure-temperature positions of the so-called triple points of supercooled H_2O and D_2O seem to be very close [45]. The difference between the densities of the corresponding H_2O and D_2O phases (the density increases by ≈11% when D substitutes for H) denotes very close molar (or atomic) densities of the isotopic analogs. In general, H_2O and D_2O have very similar phase diagrams [3–5,46], and the parameters of equilibrium transitions between various modifications of H_2O and D_2O ices, as well as the parameters of SSA and polyamorphic transitions [21,47], differ by only a few kelvins and dozens of MPa for isobaric and isothermal paths, respectively. In some cases, e.g., in the two-level far-infrared absorption spectra of amorphous ices [48] and x-ray Raman absorption spectra of water [49], the absence of isotope effects has been experimentally recorded. On the other hand, an anomalously large isotope effect in structural relaxation and the glass transition temperature of water, related by the authors with quantum effects, has recently been reported [43].

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Significant differences of relaxation properties for isotopic ice analogs are known for other phases, e.g., for ice VI [50]. The elastic constants and polycrystalline moduli (which can be considered as thermodynamic properties in many respects) of ordinary hexagonal H_2O and D_2O ices are remarkably different [51]. In our previous studies of elasticity of H_2O and D_2O ices, we have also found remarkable differences of the behavior of elastic properties during the 1h → HDA SSA and HDA → LDA polyamorphic transitions [18–21].

When H/D substitution is gradual, the situation becomes more complicated because three types of molecules (H_2O, D_2O, and HOD) define the physical properties of isotopic H_2O-D_2O solutions. The elastic properties of ordinary and supercooled liquid H_2O-D_2O solution [52], as well as many other properties (e.g., viscosity [53,54], dielectric properties [54], liquid mutual diffusivities [55]), change linearly or monotonically and close to linearly with concentration. As far as we know, solid H_2O-D_2O ices have been studied much less except for the infrared spectroscopy of crystalline equimolar HDO phases [22,25].

The aim of the current work is to study the elasticity of H_2O-D_2O solid solutions under pressure and to obtain experimentally the concentration dependences of the elastic properties. The elastic moduli, being macroscopic characteristics, should be considered as a manifestation of microscopic interatomic (intermolecular) forces, and experimental data on elastic properties along with vibrational spectra [22–33] can be used as crucial testing criteria for any empirical modeling [56,57] and quantum simulation (see, e.g., Refs. [37] and [40]) of H_2O-D_2O solid solutions. A preliminary study of an equimolar (1:1) D_2O-H_2O mixture [58] indicated nontrivial concentration dependences of the elastic moduli for some ice phases. Here we present a detailed ultrasonic study of the pressure-induced 1h → HDA and temperature-induced u-HDA → e-HDA → LDA ice polyamorphic transitions in H_2O-D_2O solid solutions for three molar concentrations (1:3, 1:1, and 3:1), comparing the results obtained with corresponding data for the isotopically pure H_2O and D_2O ices.

II. EXPERIMENT

The samples of solid H_2O-D_2O solutions were obtained by mixing 99.96% heavy water, purchased from Merck, and distilled water. The H_2O-D_2O water mixtures with molar ratios of 1:3 (25% H_2O : 75% D_2O), 1:1, and 3:1 were kept for at least two weeks, a time which was estimated as sufficient for uniform diffusive mixing of light and heavy water. Before the experiment, the sample was intensively mixed and thereafter cooled rapidly in liquid nitrogen. The cylindrical sample with a height of 8–10 mm and a diameter of 16–17 mm was placed in a high-pressure chamber of the piston-cylinder type. The surface of the ice sample was isolated from the cylindrical wall of the chamber by a thin lead foil (0.04 mm) in order to reduce friction and from the flat pistons by thin (0.02 mm) copper foil. Our previous study of pure ices [18–21] demonstrated nice coincidence with the data of other authors, e.g. [9–11], and we estimated the pressure uncertainty due to the friction at low temperatures as 0.02 GPa.

The elastic properties were studied in a pressure range of 0–2 GPa and temperature range 77–200 K using an ultrasonic high-pressure piezometer [59]. *In situ* measurements of the transverse and longitudinal ultrasound wave travel time in the sample were carried out by the pulsed method at 5 and 10 MHz, respectively. For isobaric experiments we use a natural warming of the piezometer within the temperature interval 77–200 K. We used x- and y-cut lithium niobate ($LiNb0_3$) piezoelectric transducers to generate and receive ultrasound signals. The time measurements were carried out within an accuracy of 1 ns by a "U-sonic" system based on the National Instruments PXI platform. The sample height change (and, subsequently, ultrasound velocities and density ρ from the known value ρ_0 at normal conditions) was determined by means of piston displacement sensor gauges with a precision of 5 μm. The temperature of the sample was determined within an accuracy of 1 K by four copper-Constantan thermocouples placed in the close vicinity of the high-pressure zone. Finally, the measurements resulted in accurate pressure and temperature dependences of the longitudinal v_l and transverse v_t wave velocities, which can be used to calculate the elastic properties. The bulk B and shear G elastic moduli were calculated using the standard equations for an isotropic elastic medium:

$$G = \rho v_t^2,$$

$$B = \rho v_l^2 - \frac{4}{3}\rho v_t^2.$$

The isotropic elastic medium approximation is valid when there is no texturing of a sample. In our experiments, the absence of any significant texturing of a sample may be verified, first, by the good reproducibility of quantitative results for different phases in different experiments under the same conditions; second, by coincidence of the initial and final elastic moduli for ice 1h; and third, by using different samples with different orientations with respect to the quenched pristine ingot. For each isotopic concentration the cycles of compression-decompression with subsequent isobaric warming were repeated not less than three times, and we observed the good reproducibility of experimental data. We use the standard protocol (pathway onto the p,T plane): Isothermal compression of ice 1h at 77 K up to 1.6–1.8 GPa to obtain unrelaxed u-HDA; decompression of u-HDA at 77 K; and isobaric heating of ice at 0.05 GPa up to 200 K. This experimental protocol was chosen because there are unambiguous literature experimental data about the structure and properties of ice along these pathways.

III. RESULTS AND DISCUSSION

The pressure dependences of ultrasound wave velocities for the case of compression of 1h hexagonal H_2O-D_2O, pure H_2O, and D_2O ices with subsequent pressure decrease at $T = 77$ K are shown in Fig. 1. It should be noted that the changes of ultrasound velocities are qualitatively similar for the three isotopic concentrations of ice species. An abrupt change of the sample properties under compression at $P \approx 1.1$ GPa (Fig. 1) corresponds to SSA of the 1h phase to HDA ice [9]. Actually we obtain u-HDA in these conditions [12]. Our experiments revealed no obvious shift of the transition pressure

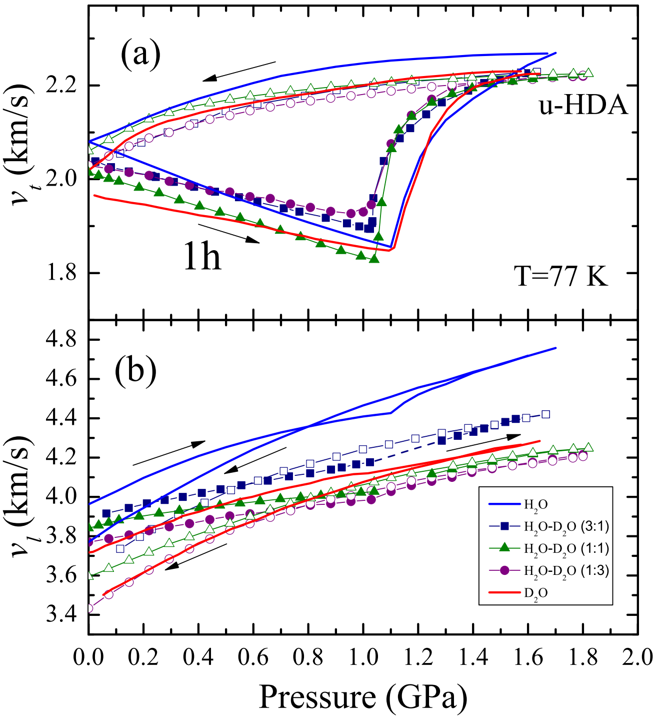

FIG. 1. (Color online) Pressure dependences of the longitudinal and transverse sound velocities for the SSA of ice 1h at 77 K. Solid symbols correspond to compression, open to decompression solid solutions. Solid lines correspond to pure H_2O and D_2O.

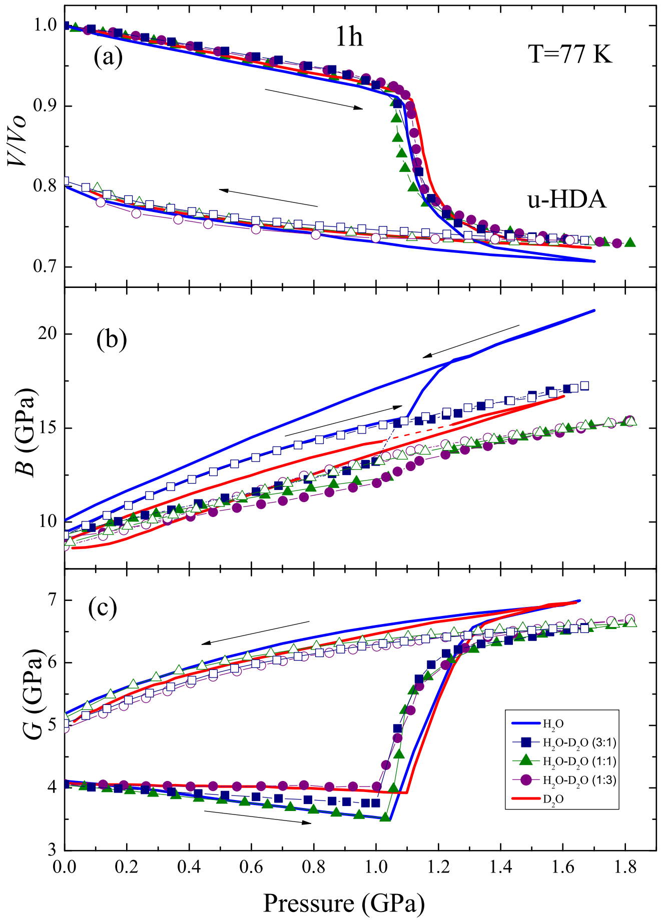

FIG. 2. (Color online) Pressure dependences of the relative volume and bulk and shear elastic moduli for the SSA of ice 1h at 77 K. Solid symbols correspond to compression, open to decompression solid solutions. Solid lines correspond to pure H_2O and D_2O.

for all H_2O-D_2O ices being studied. The 1h → HDA SSA was accompanied by a significant (≈17%) jump of the transverse ultrasound wave velocity v_t, whereas the longitudinal ultrasound velocity v_l remained almost unchanged during the transition.

The pressure dependence of the relative volume together with the calculated pressure dependences of the bulk and shear moduli are presented in Fig. 2, where the corresponding data for the isotopically pure H_2O and D_2O [18,21] are also shown. The pressure dependences of elastic B and G moduli repeat qualitatively the pressure dependences of the longitudinal and transverse sound velocities, respectively (Fig. 1). Previously [21], it has been shown that the pressure of the 1h → u-HDA transition for D_2O is 0.05 GPa higher than that for H_2O. This phenomenon can be qualitatively explained by a decrease of the amplitude of inter- and intramolecular oscillations in D_2O related to the larger effective mass of the D_2O molecule or deuterium, respectively. The transition pressures for the H_2O-D_2O solid solution are systematically lower than those for the isotopically pure ices (Fig. 2). The volume jump during the transition only slightly depends on the isotopic composition of the samples. It roughly equals 15%−16% for solid solutions and is smaller than those for H_2O (20%) and D_2O (18%). As in the pure ices there is a large jumpwise increase of the shear moduli during the 1h → u-HDA transition. On the other hand there is a significant positive jump of the bulk modulus at this transition for H_2O ice whereas there are very small changes of the bulk moduli for D_2O ice and isotopically mixed ices. As for the isotopically pure 1h ices, the common phenomenon for all mixed H_2O-D_2O 1h ices is shear elastic softening with pressure increase before SSA (Fig. 2), i.e., a pressure derivative $G'_P < 0$. Certain elastic constants, e.g., $(1/2)(c_{11} - c_{12})$ [for the hexagonal crystal system of ice 1h $(1/2)(c_{11} - c_{12}) = c_{66}$], may undergo an appreciable decrease [60]. In this respect, our experimental observation also confirms that SSA of ice 1h is associated with lattice instability [14,18,19].

Figure 3 presents the concentration dependences of the pressure derivatives B'_P and G'_P for 1h ice at $P = 0$. The pressure derivative of the bulk modulus shows a nonmonotonic concentration dependence (Fig. 3), and all H_2O-D_2O 1h solid solutions are more compressible than pure 1h H_2O and D_2O phases. All G'_P values are negative as mentioned above. The 1h solid solution with excess of D_2O has a lower absolute value of G'_P, quite close to that for the pure 1h D_2O phase (Fig. 3). Among the 1h H_2O-D_2O solid solutions the equimolar (1:1) one has the lowest shear modulus before SSA.

The concentration dependences of the bulk and shear moduli and their pressure derivatives for HDA ice at high pressures are presented in Fig. 4. All these dependences demonstrate nonmonotonic behavior with rather remarkable minima at intermediate concentrations close to the equimolar concentration 1:1. It is clear that these concentrations correspond to a maximal isotopic configurational disorder. Although we

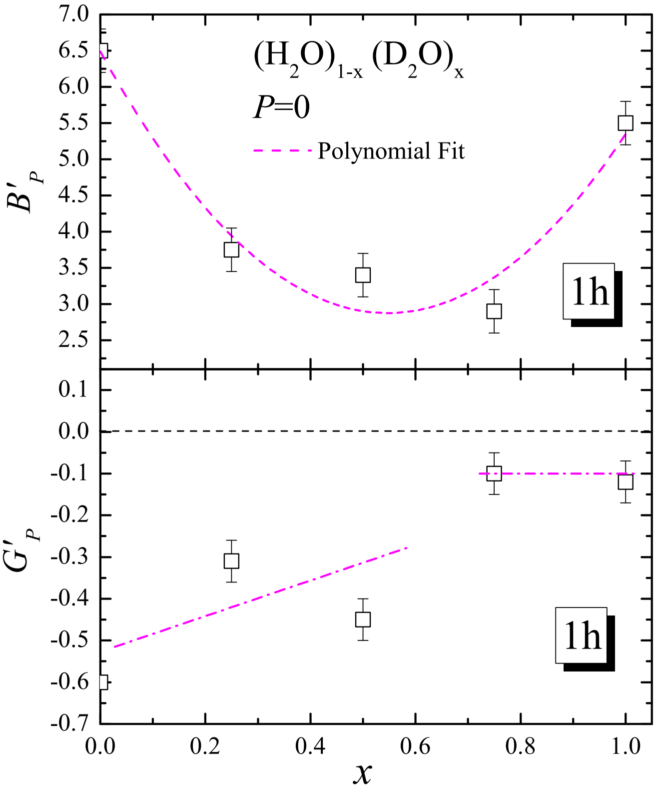

FIG. 3. (Color online) Concentration dependences of pressure derivatives of bulk and shear elastic moduli of ice 1h at 77 K and P = 0. The dashed line in the top panel is approximation by second-order polynomial. The dashed-dotted line in the bottom panel is guide for ice.

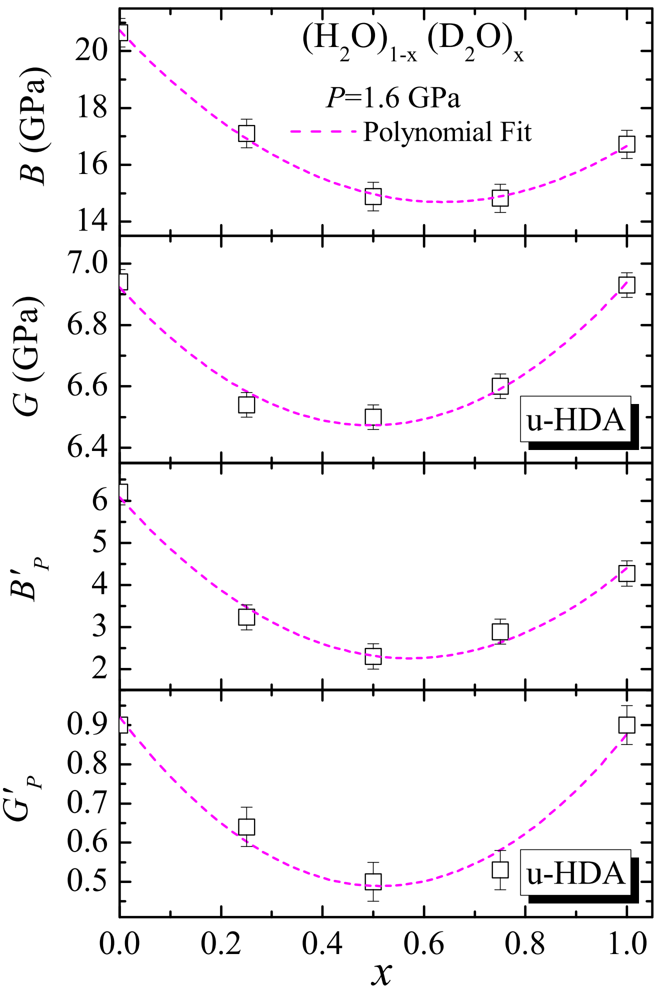

FIG. 4. (Color online) The concentration dependences of the bulk and shear elastic moduli and their pressure derivatives of u-HDA ice at 77 K and 1.6 GPa. The dashed lines are approximations by second-order polynomials.

present the data in Fig. 4 only for a particular selected pressure $P = 1.6$ GPa, qualitatively similar concentration dependences are observed starting at least from 1 GPa. The elastic properties of HDA ice at low pressures will be considered later.

It is known that heating of HDA ice (both H_2O and D_2O) at room pressure or near room pressure triggers a cascade of u-HDA → e-HDA → LDA → 1c → 1h transitions [10–16]. Our ultrasonic measurements (Fig. 5) have shown that the same transitions occur in H_2O-D_2O solid solutions, when isobaric warming of samples is started from the u-HDA state of ice. In our case warming of samples was carried out at $P = 0.05$ GPa to ensure acoustic contact in the experimental setup. Analysis of the experimental data and comparison with the well-known literature data for H_2O and D_2O, in particular [10–12,18–21] allow one to split the temperature range 77–190 K conditionally into several segments corresponding to different stages of the transition cascade in Fig. 5. The e-HDA → LDA transition is easily detected by the volume jump in the temperature interval 130–140 K, where the value of volume change is equal to ≈15% for all concentrations of H_2O and D_2O. A remarkable decrease of both ultrasound velocities, especially of the transverse one, occurs at the u-HDA → e-HDA transition. The LDA phase is characterized by a slight decrease of the longitudinal ultrasound velocity (weak growth in the case of the equimolar H_2O-D_2O solid solution) and the temperature-independent transverse ultrasound velocity. The next LDA → 1c transitions are detected in Fig. 5 by anomalies in the temperature behavior of the ultrasound velocities, while the volume changes are insignificant. According to the literature data starting from approximately 160 K ice 1c gradually transforms to ice 1h without remarkable changes of volume and ultrasound velocities.

One can mention that the works by Seidl *et al.* [15] and by Handle and Loerting [16] claim that HDA experiences a glass-liquid transition above 130 K [15] or 140 K [16] at 0.05 GPa. They consider HDA at 0.05 GPa at >140 K to be in the ultraviscous liquid state. The ultrasound study is conducted at high frequencies (5–10 MHz), and we cannot distinguish the amorphous solid from an ultraviscous liquid state. In any case, the transformation at 140 K is not a glass transition, because we have observed a large volume jump (∼15%), while at the glass transition, there is no volume jump. In the range of 110–130 K, where there is a speed-up of the expansion coefficient of the volume that correlates with the data of Nelmes *et al.* [12] an ultraviscous liquid state may exist, but we cannot make definite conclusions from our data.

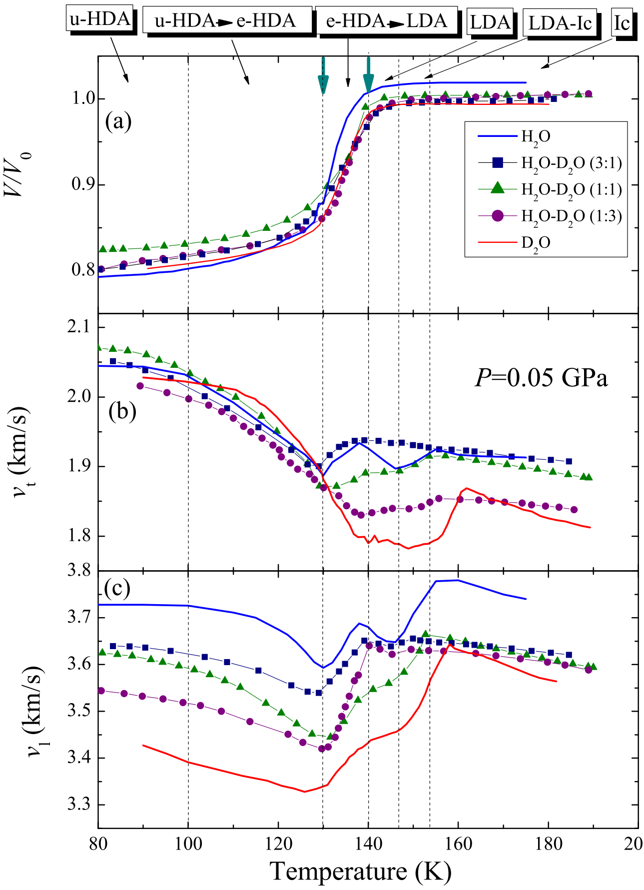

FIG. 5. (Color online) Temperature dependences of the relative volume and transverse and longitudinal sound velocities for the temperature-induced transitions at 0.05 GPa with the identification of various transition stages. Solid lines correspond to pure H_2O and D_2O. The dark cyan arrows correspond to the possible values of the glass transition temperature according to the Refs [15] and [16].

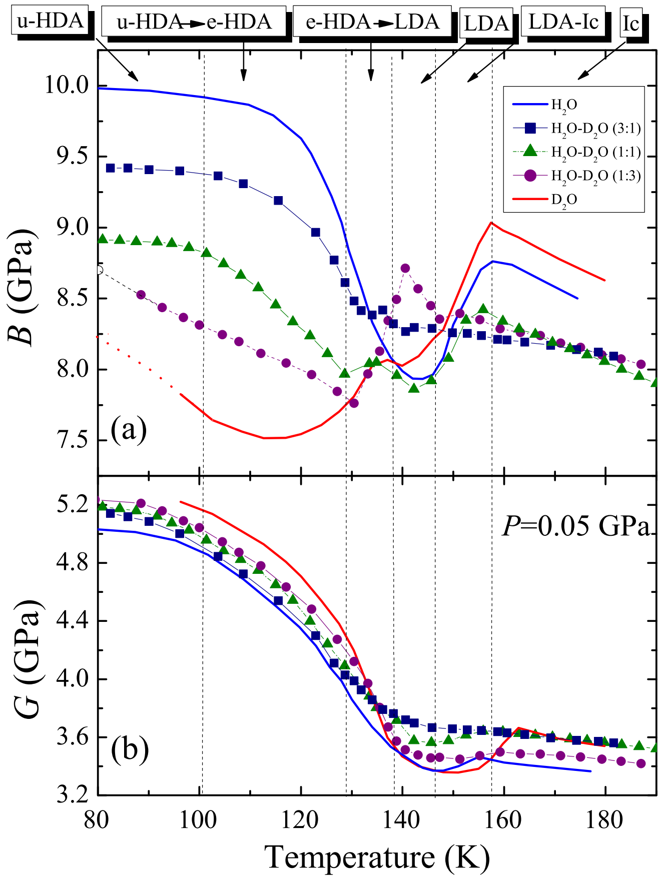

FIG. 6. (Color online) Temperature dependences of bulk and shear elastic moduli for the temperature-induced transitions at 0.05 GPa. The identification of transition stages is the same as in Fig. 5. Solid lines correspond to pure H_2O and D_2O.

The temperature dependences of the elastic moduli corresponding to experiments in Fig. 5 along with similar data for H_2O and D_2O [21] are shown in Fig. 6. The transition stages in Fig. 6 are marked exactly as in Fig. 5. There is some temperature mismatch (~5 K) between corresponding stages of the transformations for the H_2O-D_2O solid solutions and pure H_2O and D_2O ices (Fig. 6). The most pronounced isotopic effect is a change of the bulk modulus of the HDA phase. In contrast, the temperature dependences of the shear modulus for all isotopic ice mixtures are very similar (Fig. 6). Strong shear elastic softening occurs at the u-HDA → e-HDA ice transition, and there is also some softening of the bulk modulus, depending on the isotopic composition (for D_2O only, decrease of the bulk modulus changes to increase during this transition).

Figure 7 presents the concentration dependences of elastic moduli for u-HDA and 1c phases. In contrast to the high-pressure data for u-HDA ice in Fig. 4, both bulk and shear moduli of u-HDA ice demonstrate near linear concentration dependences at low pressure (Fig. 7). The bulk modulus of the 1c phase demonstrates softening for solid solutions with respect to pure isotope 1c phases, and it is clear from extrapolations of the temperature dependences in Fig. 6 that a similar trend is observed also for ice 1h. The bulk modulus of LDA ice does not demonstrate a regular concentration dependence (see Fig. 6). Probably this is related to the narrow temperature interval of existence of LDA ice, and both the e-HDA → LDA and LDA → 1*c* transitions (finishing and beginning stages, respectively) can influence the measured values. In any case the values of the bulk modulus of LDA ices for all isotope compositions are located close together in the interval ≈8−8.5 GPa.

It is important that the bulk moduli of ices 1c and 1h, which have tetrahedral order of the oxygen sublattice as the skeleton of the structure, demonstrate softening (i.e., increase of compressibility) for solid solutions with respect to the isotopically pure components [Figs. 6 and 7(c)], and this trend continues with pressure increase, at least for ice 1h (Fig. 3). Tetrahedral order in this case means that each oxygen atom has oxygen nearest-neighbor atoms forming a regular tetrahedron in ice 1c or a tetrahedron that is very close to regular in ice 1h. The bulk modulus softening can result from any fluctuations of O-O bond lengths. In our case, such fluctuations would result from a configurational isotopic disorder of hydrogen and deuterium atoms at O-O bonds, and this effect is clearly of quantum nature. The observed phenomenon of the bulk modulus softening in solid solutions seems to be

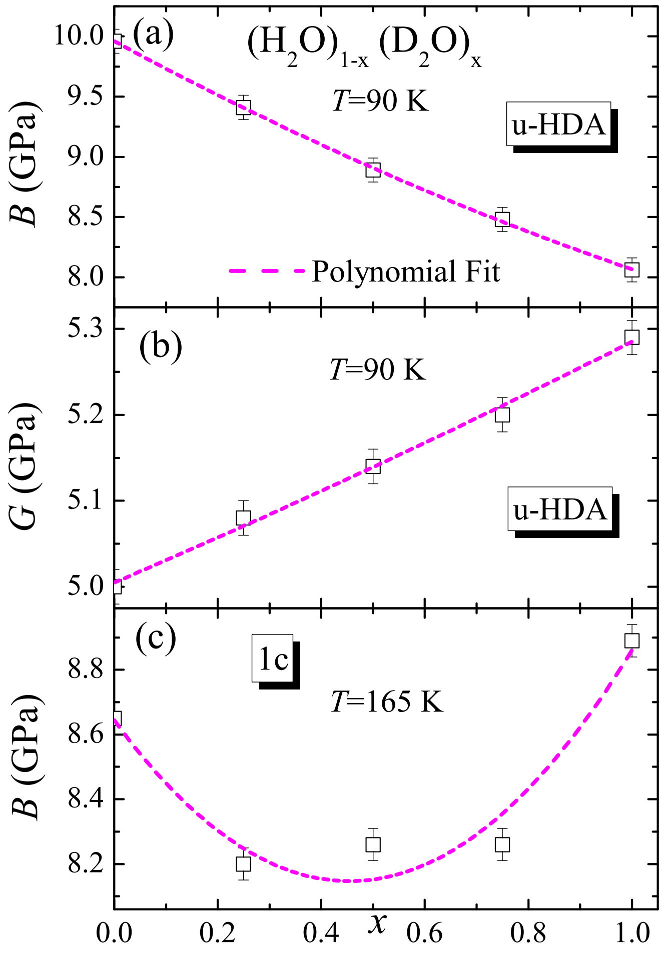

FIG. 7. (Color online) The concentration dependences of bulk and shear moduli of the u-HDA ice at 90 K and bulk modulus of ice 1c at 165 K ($P = 0.05$ GPa).

more general for tetrahedrally ordered substances. A similar effect of elastic softening has been observed for solid solutions between germanium with diamondlike structure and gallium antimonide with sphaleritelike structure (the biatomic analog of the diamond structure) [61]. Both covalent components are tetrahedrally ordered. Moreover, amorphous Ge-GaSb solid solutions were systematically more compressible than their crystalline counterparts, although the densities of amorphous and crystalline solid solutions with the same composition were nearly equal [61,62]. So any disorder in tetrahedrally ordered structures may cause elastic softening. A comparison of values of the bulk modulus for the tetrahedrally ordered LDA, 1h, and 1c ices [Fig. 6(a)], $B(\mathrm{LDA}) < B(1\mathrm{h}) < B(1c)$, suggests the same trend relating disorder and elasticity (here, ice 1h is less ideal with respect to ice 1c due to relaxation of the lattice parameter ratio in the hexagonal structure). A similar relation is observed for the shear elastic modulus [Fig. 6(b)].

Special interest is directed to the elasticity of u-HDA ice. First, the concentration dependences of the elastic moduli for the HDA phase are monotonic at low pressures (Fig. 7), and there is a pronounced change of the bulk modulus, ≈20%, between H_2O and D_2O u-HDA ices. Second, at high pressures (>1 GPa), the concentration dependences of both elastic moduli significantly change (Fig. 4), demonstrating elastic softening for H_2O-D_2O solid solutions, as for the bulk modulus of tetrahedrally ordered phases at low pressure. Probably such behavior is related to specific structural features of HDA ice (see, e.g., Refs. [13,63] and references therein). Each oxygen atom is fully hydrogen bonded with a local tetrahedral arrangement of the oxygen neighbors, and, under pressure, there are some similarities of the elasticity of the HDA solid solutions and the low-pressure tetrahedrally ordered phases. However, the structural difference between LDA and HDA ices becomes significant beyond the first-neighbor oxygen shell. This means, in particular, that the majority of the oxygen nearest-neighbor tetrahedrons in HDA ice are remarkably distorted from the regular form. At low pressures HDA ice is less stable than LDA ice. In other words, HDA ice is "metastable" in the conditional low-temperature "thermodynamics" of ice polyamorphism. This may result in significant structural relaxation in HDA ice during depressurizing and further heating, and, in turn, the isotopic composition may significantly influence this relaxation. In any case, our experimental data on the elasticity of HDA ice give evidence in favor of this viewpoint.

IV. CONCLUDING REMARKS

The presented experimental data are significant as tabular data, of course. They also prove that the pressure-temperature transition behavior of H_2O-D_2O solid solutions and the mechanisms of their transitions are very similar to those of isotopically pure H_2O and D_2O ices. Nevertheless, the main result of the work concerns the effect of H/D substitution on the elasticity of ice phases. The isotopic differences of elastic properties are evidently related to structural differences, which appear, first of all, due to the significantly different quantum dynamics of hydrogen and deuterium. In this respect, the presented experimental data should be considered as a crucial test for the functionality of theoretical models. It should be noted that the technique of isotope substitution is often used in neutron diffraction studies and the structures of H_2O, HDO, and D_2O water and ices are considered as almost the same. This is true at high temperatures; however, at lower temperature the structural differences may be significant (see also in this respect the data of [42]). The key elastic phenomena observed in the set of pure H_2O and D_2O ices and their solid solution include the following: (1) decrease of the shear elastic modulus of ice 1h with pressure and the remarkable concentration dependence of its pressure derivative G'_P; (2) softening of the elastic moduli and their pressure derivatives at intermediate H_2O and D_2O concentrations for several particular cases; (3) remarkably different isotopic concentration dependences of the elastic moduli at low and high pressures in the case of HDA ices. Those theoretical simulations that adequately describe the presented experimental data may explain the nature of the observed effects.

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[1] T. Bartels-Rausch, V. Bergeron, J. H. E. Cartwright, R. Escribano, J. L. Finney, H. Grothe, P. J. Gutiérrez, J. Haapala, W. F. Kuhs, J. B. C. Pettersson, S. D. Price, C. I. Sainz-Díaz, D. J. Stokes, G. Strazzulla, E. S. Thomson, H. Trinks, and N. Uras-Aytemiz, Rev. Mod. Phys. **84**, 885 (2012).

[2] A. D. Fortes and M. Choukroun, Space Sci. Rev. **153**, 185 (2010).

[3] E. Yu. Tonkov, *High Pressure Phase Transformations, A Handbook*, Vol. 2 (Gorgon and Breach, Philadelphia, 1992; Metallurgiya, Moscow, 1988), Vol. 2.

[4] V. F. Petrenko and R. W. Whitworth, *Physics of Ice* (Oxford University Press, Oxford, 2002).

[5] M. Chaplin, Water Structure and Science, http://www.lsbu.ac.uk/water

[6] O. Mishima and H. E. Stanley, Nature (London) **396**, 329 (1998).

[7] H. E. Stanley, S. V. Buldyrev, O. Mishima, M. R. Sadr-Lahijany, A. Scala, and F. W. Starr, J. Phys.: Condens. Matter **12**, A403 (2000).

[8] T. Loerting, K. Winkel, M. Seidl, M. Bauer, C. Mitterdorfer, P. H. Handle, C. G. Salzmann, E. Mayer, J. L. Finney, and D. T. Bowron, Phys. Chem. Chem. Phys. **13**, 8783 (2011).

[9] O. Mishima, L. D. Calvert, and E. Whalley, Nature (London) **310**, 393 (1984).

[10] O. Mishima, L. D. Calvert, and E. Whalley, Nature (London) **314**, 76 (1985).

[11] O. Mishima, J. Chem. Phys. **100**, 5910 (1994).

[12] R. J. Nelmes, J. S. Loveday, Th. Strässle, C. L. Bull, M. Guthrie, G. Hamel and S. Klotz, Nat. Phys. **2**, 414 (2006).

[13] T. Loerting and N. Giovambattista, J. Phys.: Condens. Matter **18**, R919 (2006).

[14] T. Loerting, V. V. Brazhkin, and T. Morishita, in *Advances in Chemical Physics*, Vol. 143, edited by S. A. Rice (Wiley, New York, 2009), p. 29.

[15] M. Seidl, K. Amann-Winkel, P. H. Handle, G. Zifferer, and T. Loerting, Phys. Rev. B **88**, 174105 (2013).

[16] P. H. Handle and T. Loerting, Phys. Chem. Chem. Phys. **17**, 5403 (2015).

[17] T. Loerting, V. Fuentes-Landete, P. H. Handle, M. Seidl, K. Amann-Winkel, C. Gainaru, and R. Böhmer, J. Non.-Cryst. Solids **407**, 423 (2015).

[18] E. L. Gromnitskaya, O. V. Stal'gorova, V. V. Brazhkin, and A. G. Lyapin, Phys. Rev. B **64**, 094205 (2001).

[19] E. L. Gromnitskaya, O. V. Stal'gorova, and V. V. Brazhkin, JETP Lett. **85**, 200 (1997).

[20] A. G. Lyapin, O. V. Stal'gorova, E. L. Gromnitskaya, and V. V. Brazhkin, JETP **94**, 283 (2002).

[21] E. L. Gromnitskaya, O. V. Stal'gorova, A. G. Lyapin, V. V. Brazhkin, and O. B. Tarutin, JETP Lett. **78**, 488 (2003).

[22] D. F. Horning, H. F. White, and F. P. Reding, Spectrochim. Acta **12**, 338 (1958).

[23] J. E. Bertie and E. Whalley, J. Chem. Phys. **46**, 1271 (1967).

[24] J. Marti, J. A. Padró, and E. Guàrdia, J. Mol. Liq. **62**, 17 (1994).

[25] E. Katoh, M. Song, H. Yamawaki, H. Fujihisa, M. Sakashita, and K. Aoki, Phys. Rev. B **62**, 2976 (2000).

[26] P. T. T. Wong and E. Whalley, J. Chem. Phys. **64**, 2359 (1976).

[27] K. R. Hirsch and W. P. Holzapfel, J. Chem. Phys. **84**, 2771 (1986).

[28] D. D. Klug, O. Mishima, and E. Whalley, J. Chem. Phys. **86**, 5323 (1987).

[29] M. H. Brooker, G. Hancock, B. C. Rice, and J. Shapter, J. Raman Spectrosc. **20**, 683 (1989).

[30] A. I. Kolesnikov, J.-C. Li, D. K. Ross, V. V. Siritzin, O. I. Barkalov, E. L. Bokhenkov, and E. G. Ponyatovskii, Phys. Lett. A **168**, 308 (1992).

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

[32] J.-C. Li, C. Burnham, A. I. Kolesnikov, and R. S. Eccleston, Phys. Rev. B **59**, 9088 (1999).

[33] J. Li and A. I. Kolesnikov, J. Mol. Liq. **100**, 1 (2002).

[34] C. A. Chatzidimitriou-Dreismann, U. K. Krieger, A. Moller, and M. Stern, Phys. Rev. Lett. **75**, 3008 (1995).

[35] C. A. Chatzidimitriou-Dreismann, T. A. Redah, R. M. F. Streffer, and J. Mayers, Phys. Rev. Lett. **79**, 2839 (1997).

[36] L. E. Bove, S. Klotz, A. Paciaroni, and F. Sacchetti, Phys. Rev. Lett. **103**, 165901 (2009).

[37] H. Gai, G. K. Schenter, and B. C. Garret, Phys. Rev. B **54**, 14873 (1996).

[38] A. Pietropaolo, R. Senesi, C. Andreani, A. Botti, M. A. Ricci, and F. Bruni, Phys. Rev. Lett. **100**, 127802 (2008).

[39] A. K. Soper and C. J. Benmore, Phys. Rev. Lett. **101**, 065502 (2008).

[40] J. A. Morrone and R. Car, Phys. Rev. Lett. **101**, 017801 (2008).

[41] A. Giuliani, F. Bruni, M. A. Ricci, and M. A. Adams, Phys. Rev. Lett. **106**, 255502 (2011).

[42] R. T. Hart, C. J. Benmore, J. Neuefeind, S. Kohara, B. Tomberli, and P. A. Egelstaff, Phys. Rev. Lett. **94**, 047801 (2005).

[43] C. Gainaru, A. L. Agapov, V. Fuentes-Landete, K. Amann-Winkel, H. Nelson, K. W. Köster, A. I. Kolesnikov, V. N. Novikov, R. Richert, R. Böhmer, T. Loerting, and A. P. Sokolov, Proc. Natl. Acad. Sci. USA **111**, 17402 (2014).

[44] J. Urquidi, C. J. Benmore, J. Neuefeind, B. Tomberli, C. A. Tulk, M. Guthrie, P. A. Egelstaff, and D. D. Klug, J. Phys.: Condens. Matter **15**, 3657 (2003).

[45] O. Mishima, Phys. Rev. Lett. **85**, 334 (2000).

[46] G. Weck, J. Eggert, P. Loubeyre, N. Desbiens, E. Bouasseau, J.-B. Maillet, M. Mezouar, and M. Hanfland, Phys. Rev. B **80**, 180202 (2009).

[47] M. A. Floriano, Y. P. Handa, D. D. Klug, and E. Whalley, J. Chem. Phys. **91**, 7187 (1989).

[48] N. I. Agladze and A. J. Sievers, Phys. Rev. Lett. **80**, 4209 (1998).

[49] J. S. Tse, D. M. Shaw, D. D. Klug, S. Patchkovskii, G. Vankó, G. Monaco, and M. Krisch, Phys. Rev. Lett. **100**, 095502 (2008).

[50] G. P. Johari and E. Whalley, J. Chem. Phys. **70**, 2094 (1979).

[51] U. Mitzdorf and D. Helmreich, J. Acoust. Soc. Am. **49**, 723 (1971).

[52] O. Conde, J. Teixeira, and P. Papon, J. Chem. Phys. **76**, 3747 (1982).

[53] J. Kestin, N. Imaishi, S. H. Nott, J. C. Nieuwoudt, and J. V. Sengers, Physica A **134**, 38 (1985).

[54] U. Kaatze, Chem. Phys. Lett. **203**, 1 (1993).

[55] M. L. S. Matos Lopes and C. A. Nieto de Castro, Int. J. Thermophys. **7**, 699 (1986).

[56] C. Vega, E. Sanz, and J. L. F. Abascal, J. Chem. Phys. **122**, 114507 (2005).

[57] C. Vega and J. L. F. Abascal, Phys. Chem. Chem. Phys. **13**, 19663 (2011).

[58] E. L. Gromnitskaya, A. G. Lyapin, O. V. Stal'gorova, I. V. Danilov, and V. V. Brazhkin, JETP Lett. **96**, 789 (2013).

[59] O. V. Stal'gorova, E. L. Gromnitskaya, D. R. Dmitriev, and F. F. Voronov, Instrum. Exp. Tech. **39**, 880 (1996).

[60] Th. Strässle, A. M. Saitta, S. Klotz, and M. Braden, Phys. Rev. Lett. **93**, 225901 (2004).

[61] A. A. Stolbov, A. G. Lyapin, S. V. Popova, V. V. Brazhkin, E. L. Gromnitskaya, and O. V. Stal'gorova, High Press. Res. **23**, 187 (2003).

[62] V. V. Brazhkin, A. G. Lyapin, V. A. Goncharova, O. V. Stal'gorova, and S. V. Popova, Phys. Rev. B **56**, 990 (1997).

[63] D. T. Bowron, J. L. Finney, A. Hallbrucker, I. Kohl, T. Loerting, E. Mayer, and A. K. Soper, J. Chem. Phys. **125**, 194502 (2006).