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CALORIMETRIC STUDY OF TRANSITION PHENOMENA IN MOLECULAR SOLIDS

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Principle and technical development of low temperature calorimetry are described. Typical experimental results obtained by our group at Osaka University over the four decades are given. These include phase transitions in equilibrium crystals and glass transitions in non-equilibrium frozen-in disordered solids including crystals. It can be concluded that the glass transitions observed exclusively in liquids so far are just one example of transitions that must be of wide occurrence in solids arising from freezing of relevant degrees of freedom. Interplay between the phase and glass transitions in crystals is discussed in relation to useful dopant that may accelerate some molecular motions that had failed to maintain equilibrium at low temperatures.

Keywords: *glass transition, glassy crystals, glassy liquids, phase transition, structural relaxation*

Introduction

There have been developed various physical and chemical methods in producing amorphous solids other than the traditional liquid cooling. Vapor deposition, milling of crystals, and others belong to the former, while dehydration of hydrate crystals, gelation, chemical precipitation are categorized to the latter. Secrist and Mackenzie [1] have raised a question as to whether these amorphous solids can be regarded as glasses or not. The question is related to the multifarious nature of classification of the substances. Division of the states of aggregation of molecules into gases, liquids and solids is based on mechanical properties. Further division of the solids into amorphous and crystalline states is based obviously on the structural aspect. Division of a liquid into glassy and undercooled liquid states is based on nonergodic and ergodic nature derived from thermodynamic reasoning. The question was important, because two words ‘amorphous solids’ and ‘glasses’ had been used in literatures without clear distinction. One experimental method to answer this question is to detect in amorphous solids possible existence of the glass transition and residual entropy that have been believed to be characteristic of glasses.

When we have developed an adiabatic calorimeter around early 1960s, the main research subject was phase transitions observed in molecular crystals. The subject was fascinating because the transitions sometimes induced drastic change in the elastic, electric and magnetic properties [2]. We have encountered in some cases spontaneous change in calorimetric temperature during the measurements not only for liquids but also for crystals. The phenomena were regarded as enthalpy relaxation associated with irreversible stabilization of the systems. The observations motivated us to undertake a series of experiments for frozen-in disordered solids.

Apparatus and procedure

Figure 1 represents three typical adiabatic calorimeters developed by us. The left-hand calorimeter was of a standard immersion type with two adiabatic shields for easy realization of adiabatic condition [3]. A small transfer siphon was attached to this calorimeter whenever a rapid cooling of sample is required. Liquid nitrogen or hydrogen was poured directly into the vacuum space surrounding the central calorimetric cell so as to give a cooling rate more than $-100\ \mathrm{K\ min^{-1}}$. Glassy state of isopentane was produced by this way and its residual entropy along with T_g value was determined successfully. The middle one is an adiabatic calorimeter with a built-in cryo-refrigerator [4]. Temperatures as low as 13 K were realized for a long time without supply of liquid hydrogen. The calorimeter is suitable for annealing experiment over an extended time at low temperatures.

The right-hand one is a miniaturized adiabatic calorimeter [5]. In the old times, more than 10 g of high purity sample was necessary for producing heat capacity data that guarantee the accuracy of 1% below 20 K, 0.5% between 20 and 50 K, and 0.3% above 50 K. This large amount limited the target substance for the calorimetric experiment. The new calorimeter is of twin

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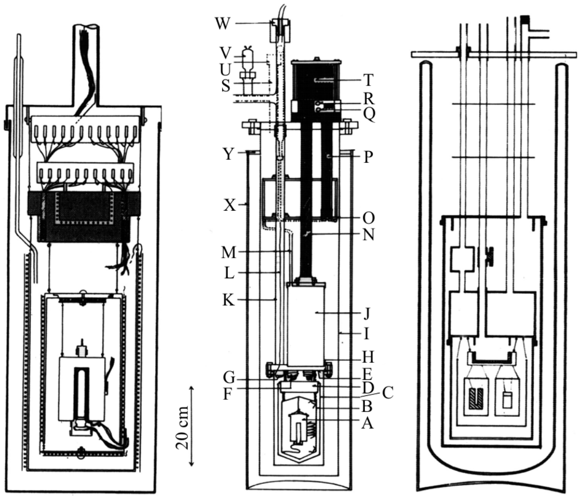

Fig. 1 Typical adiabatic calorimeters developed by thermodynamic group in Osaka University

type. A resistance thermometer is removed from the calorimetric cell, and is placed into a second cell kept always the same temperature with that of the calorimetric cell by using fine thermocouples combined with a negative feedback system. This arrangement eliminates completely a self-heating effect of thermometer that becomes important for a small quantity of sample. This temperature-transfer system enables us to derive the necessary data without loss of the claimed accuracy for a sample less than 1 g.

The process of heat capacity determination is composed of the equilibration period and the energizing period. In the former period, the calorimetric temperature is measured as a function of time. While in the latter period, a definite amount of electric energy is supplied to raise the calorimetric temperature. For any equilibrium systems, the calorimetric temperature is always constant during the equilibration period. However this does not happen for a non-equilibrium system that exhibits enthalpy stabilization at some temperature range where the corresponding relaxation time τ of the system becomes comparable to the experimental time, as in the case of a liquid around its T_g. Change in the calorimetric temperature during equilibration period can be expressed by the following equation.

$$T(t)=a+bt+c\exp[(-t/\tau)^{\beta}] \tag{1}$$

where τ is the average relaxation time, β the non-exponential parameter defined by the Kohlrausch, and Williams and Watts [6]. The second term bt represents the temperature drift rate due to a residual heat leakage and is of the order of several mK h^{-1} in most of the temperature range. The equation enables us to determine experimentally the kinetic parameters, τ and β, governing the relaxation. The time domain covered by the methods is 0.1 ks~1 Ms [7].

Results and discussions

Phase transition in equilibrium crystals

Many of the interesting properties of hydrogen-bond (HB) crystals derive from the disorder of proton that is located on a double minimum potential in a HB. At high temperature, the water molecules reorient rapidly in the crystal, as is evidenced by the large dielectric constant. There are many HB crystals that undergo phase transitions on cooling arising from disorder–order change in the proton configurations of the systems. Figure 2 shows the heat capacities of $SnCl_2{\cdot}2H_2O$, $K_4[Fe(CN)_6]{\cdot}3H_2O$ and $Cu(HCOO)_2{\cdot}4H_2O$, respectively [8]. All these crystals have layer structures in which layers of the salt component are held together by layers of water molecules hydrogen-bonded to each other. The HB network of $K_4[Fe(CN)_6]{\cdot}3H_2O$ incorporates N atoms of $[Fe(CN)_6]^{4-}$ ions, but only O atoms of water molecules are involved in the network of the remaining hydrate crystals. The two-dimensional HB networks are schematically drawn below each heat capacity curve.

All the crystals undergo phase transitions due to the order–disorder of proton configuration. The heat capacity anomaly associated with the transition differs much to each other, depending strongly on the topology of each HB network. The phase transition in $Cu(HCOO)_2{\cdot}4H_2O$ is of the first-order nature for which the Clausius–Clapeyron equation can be applied. The one observed in $K_4[Fe(CN)_6]{\cdot}3H_2O$ is of the second-order nature, for which the Ehrenfest equation holds. $SnCl_2{\cdot}2H_2O$ exhibits a typical critical behaviour. The heat capacity diverges symmetrically from both sides of T_c=234.47 K. The critical indices α for the heat capacity divergence is defined as follows.

$$\Delta C_p(T)=(A/\alpha)[(|T-T_c|/T_c)^{-\alpha}-1] \tag{2}$$

where A is the critical amplitude. The index was determined from high-resolutional heat capacity measurement to be α_+=0.492 and α_-=0.492. The sign + means for the high temperature side and – for low temperature side of T_c, respectively. The symmetric divergence of heat capacity (α_+/α_-=1) is a trademark of two-dimensionally interacting system.

Reorientational motion of a water molecule in HB system is possible only by simultaneous motions of the neighboring molecules. The highly cooperative nature of the motion comes from the severe constraints imposed by the ice conditions [9]. Shaded area drawn in each network is such a region in which the cooperative motion takes place. In the case of $Cu(HCO_2)_2{\cdot}4H_2O$, the shaded area extends from one end of crystal surface to another end. Any fluctuation in the proton configurations is not allowed until the water molecules acquire enough amount of thermal energy at the transition temperature. $K_4[Fe(CN)_6]{\cdot}3H_2O$ has an isolated cooperative

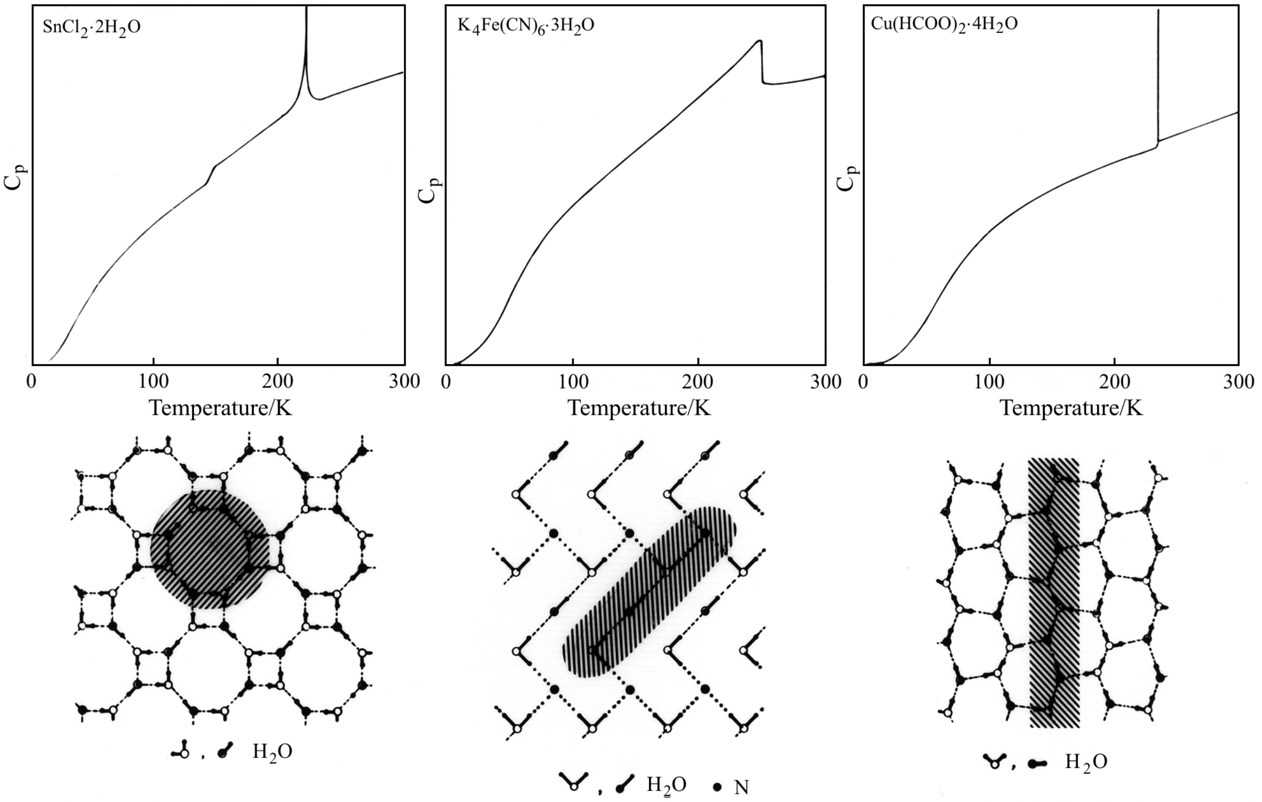

Fig. 2 Heat capacities and phase transitions observed in three hydrate crystals along with schematic drawing of each hydrogen-bonded network

region in which only four configurations can be possible by the reorientational motion. The entropy of transition is about *R*ln4 in this case. The smallest cooperative region in $SnCl_2·2H_2O$ crystal is the eight-membered HB ring. Thus fluctuation among many proton configurations all over the whole crystal will lead to the critical behavior of the heat capacity anomaly.

Glass transition in amorphous solids

It is known that chemical reactions of As^{3+} and Sb^{3+} aqueous solution with H_2S gas produce amorphous precipitates As_2S_3(am) and Sb_2S_3(am), respectively. These amorphous solids turned out to exhibit clearly glass transition T_g at essentially the same temperatures with those of liquid-cooled samples [10]. Likely, amorphous anhydride $Mg(CH_3COO)_2$(am) prepared by dehydration of its tetrahydrate crystal exhibited T_g at 400 K. The glass transition was followed immediately by crystallization on further heating. Water molecules are important ingredient in constructing the lattice of hydrate crystals. If the water molecules are extracted rapidly by evacuation at room temperature, being well below hypothetical T_g of the formed amorphous anhydride, the lattice will be destroyed to form a solid in glassy state.

Vapor deposition is a powerful method for amorphization of molecular liquids with poor glass-forming ability. Thermal energy of the constituting molecules can be extracted effectively in a molecule-by-molecule fashion without passage of the crystallization-dangerous-region in the corresponding liquid. Substance with the lowest molar mass vitrified by the method was propene C_3H_6. The T_g value determined by DTA was 55 K and was the same as that of the liquid-quenched sample.

Solid-state amorphization by mechanical milling of crystals is one of the low temperature routes for vitrification that is useful for a thermally unstable substance. The technique was used successfully to binary metallic systems for producing amorphous alloys. Contrary to the metallic systems, molecular crystal can be vitirified even in a single system. The T_g value and the enthalpy of crystallization were found to increase asymptotically with the milling time [11]. When some kinds of two crystalline samples were milled simultaneously, the resulting amorphous solids exhibited single T_g depending on the composition. This showed clearly a formation of ‘molecular alloys’ in glassy state. The formation of alloys is possible for a pair of molecular crystals that are unable to form any solid solutions under the equilibrium condition. The milling technique will provide a new way for formation of functional materials in molecular assembly.

In this way, all the amorphous solids prepared by non-equilibrium processing have proven to show T_g. These observations clearly answer the question raised by Secrist and Mackenzie mentioned above. From the scientific viewpoint, glassy or vitreous state is defined as a frozen-in non-equilibrium amorphous solid realized below T_g.

Heat capacity, residual entropy and relaxation of liquids

Figure 3 shows the heat capacity and entropy of isopropylbenzene [12]. The heat capacity of liquid is much higher than its crystal because the configurational degrees of freedom are easily excited with increasing temperature in the liquid but not in the crystal. Thus the heat capacity of this fragile liquid undergoes a large drop on vitrification at primary T_g or $T_{g\alpha}$. On further cooling, the heat capacity exhibits another tiny drop at secondary T_g or $T_{g\beta}$. The drop is quite small but the existence of $T_{g\beta}$ is clearly supported by systematic change in the rates of spontaneous temperature drifts, being exothermic below T_g followed by endothermic above T_g on heating. The entropy of liquid exhibits a bend corresponding to the heat capacity drop at $T_{g\alpha}$ and results in the residual entropy S_0 that measures the frozen-in disorder.

The extrapolated entropy of the equilibrated ideal liquid intersects the entropy of the crystal at the Kauzmann temperature T_K [13], at which the configurational entropy of the liquid vanishes. Further extrapolation beyond T_K produces a glass with negative configurational entropy. In order to save this entropy catastrophe, Gibbs and DiMarzio [14] proposed a thermodynamic second-order phase transition at T_K, and suggested that the actual T_g is a kinetic manifestation of the underlying phase transition. Many other models have been suggested to avoid the entropy crisis since then. Johari [15] proposed that the heat capacity of an equilibrium liquid will decrease along a sigmoid path stretched over a broad temperature range from above T_g to 0 K. He also suggested an experimental resolution for discriminating these models.

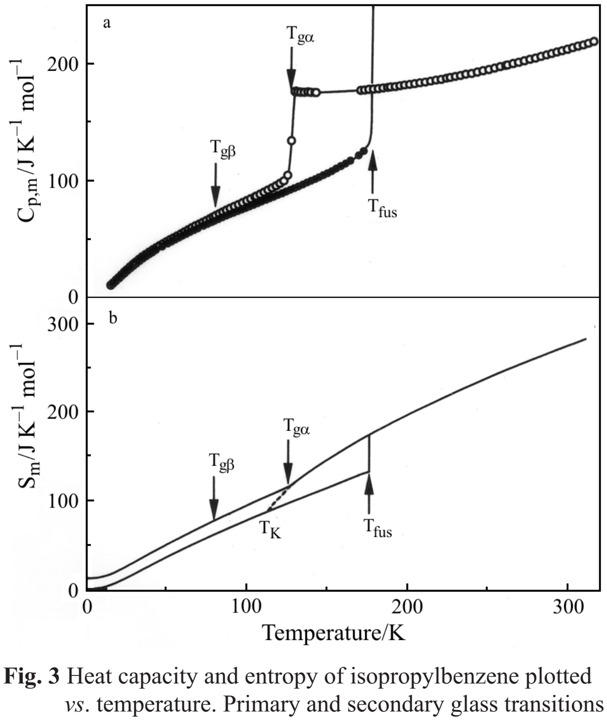

Fig. 3 Heat capacity and entropy of isopropylbenzene plotted *vs*. temperature. Primary and secondary glass transitions are denoted $T_{g\alpha}$ and $T_{g\beta}$, respectively

The enthalpy relaxation process for glasses can be studied by following the revolution of the glassy structure from a non-equilibrium state into the equilibrium after a step change in T or p. Relaxation functions for the enthalpy of 1-butene were determined in two ways. One sample was prepared by a rapid-cooling by $-\Delta T_j$, and the other by a rapid-heating by ΔT_j from the equilibrium liquid, respectively. The former sample has an excess configurational enthalpy at the initial stage and the structural relaxation accompanies spontaneous exothermic temperature drift under an adiabatic condition. The latter has negative initial sign and shows endothermic drift [16].

It turned out that the relaxation process for 1-butene measured at 58 K was quite asymmetric with respect to the sign of initial departure. The values, τ=6.52 ks and β=0.56, and the ones, τ=5.96 ks and β=0.84, were derived for the exothermic and endothermic processes, respectively. The rate of structural recovery differs between the positive and negative values of ΔT_j, depending on whether the relaxation is a structure-breaking or structure-forming process. Fujimori *et al.* [17] extended this work by changing the amount of initial departure ΔT_j for glycerol and other substances, and found that the parameter changed linearly with the value ΔT_j. The slope showed a slight change at ΔT_j=0, at which the value β will reflect the distribution of relaxation times of the equilibrium liquid. Similar experiment has been done for amorphous butyronitrile prepared by liquid cooling and vapor deposition [18].

Glass transition in crystal, glassy crystals

Some molecular crystals fuse in two steps, either through the liquid crystal or orientationally disordered crystal (ODC) phases. These mesophases have the entropy close to those of isotropic liquids. Most of the ODC have fcc or bcc lattice with molecules possessing a great deal of orientational disorder. If such a phase is cooled rapidly by avoiding the transformation into an ordered crystal, the undercooled disordered phase undergoes freezing-in process at a temperature at which the relevant relaxation time τ

crosses the experimental time, as in the case of ordinary glasses. Particularly the glassy states of crystals designated as ‘glassy crystals’ are interesting because glasses and crystals are two extremes in our concept of structural regularity in solids.

Cyclohexanol forms an fcc lattice below T_{fus}. The high crystallographic symmetry arises entirely from orientational disorder (OD) of the molecule that has only mirror symmetry. When the fcc phase is cooled rapidly, the undercooled phase exhibits $T_{\mathrm{g}\alpha}$ at about 150 K and has a residual entropy [10]. The behavior of enthalpy relaxation is unable to discriminate in all aspects from that of ordinary glasses only except for the existence of a long-range positional order in cyclohexanol crystal. The heat-capacity tail below T_g is noticeable. The long tail below T_g causes the S_c to decrease over a wide range of temperature. This phenomenon has been observed more or less in many glassy solids and the effect to the residual entropy of cyclohexanol was discussed in details [19].

In the case of ethanol, two kinds of $T_{\mathrm{g}\alpha}$ were observed for its liquid and its metastable OD phases, respectively. Both of the glass transitions take place at essentially the same temperature of 97 K. Two glass transitions can occur for different phases of one and the same substance. This observation clearly shows a wide occurrence of the glass transition in condensed phases, irrespective of positional disorder. Table 1 lists example of glassy crystals and their T_g values.

The situation is not limited to metastable undercooled phase of crystal. Observation of residual entropy in ice I_h is the most familiar example of freezing-out of molecular motions in the stable crystal. The half-hydrogen model proposed by Pauling cannot be an equilibrium structure that satisfies the third law of thermodynamics, but absence of any anomalous heat capacity ascribable to an ordering transition has puzzled many scientists for a long time [9]. The dielectric and enthalpy relaxation times of ice, turned out to lie on the same straight line in an Arrhenius plot [20]. Extrapolation of these data to 60 K, a hypothetical ordering temperature proposed by Pitzer and Polissar [21], gave a value of 10^{13} s for τ. It must be this geological time that hindered the crystal from reaching an ordered phase of ice I_h in our laboratory time. Onsager [22] suggested to use some impured ice samples for inducing the expected ordered phase. The impurity might hopefully relax the severe constraints ‘ice relues’ imposed to the cooperative reorientational motion of water molecules.

A minute amount of KOH doped into the ice lattice was found to accelerate dramatically the reorientational motion of water dipoles [20]. Thus, an ice sample doped with KOH in the mole fraction of $2\cdot10^{-5}$ exhibited a first-order phase transition at 72 K, which re-

Table 1 Glass transition temperature T_g of various glassy crystals

Metastable phase	T_g/K	Stable phase	T_g/K
thiophene	37	thiophene	42
2,3-dimethylbutane	76	buckminsterfullerene C_{60}	87
isocyanocyclohexanol	55	β-cyclodextrin·$11H_2O$	150
	130	ethylene oxide·$6.86H_2O$	85
	160	tetrahydrofuran·$17H_2O$	85
$CFCl_2$–$CFCl_2$	60	acetone·$17H_2O$	90
	90	CO	18
	130	RbCN	30
ethanol	90	$CsNO_2$	42
cyclohexene	92	$TlNO_2$	60
	93	$SnCl_2\cdot2H_2O$	150
cycloheptane	100	$SnCl_2\cdot2D_2O$	155
	100	H_2O (hexagonal)	105
	93	H_2O (cubic)	140
cycloheptatriene	106	D_2O (hexagonal)	115
cycloheptanol	135	pinacol·$6H_2O$	155
cyclohexanol	150	H_3BO_3	290
$Cs_{0.7}Tl_{0.3}NO_2$	48	D_3BO_3	298
		lysozyme	ca. 150
C_2Cl_6 in thiourea adduct	59	myoglobin	ca. 170

T_g value of protein crystal depends strongly on the amount of hydrate water moved a substantial fraction of the residual entropy and changed the lattice symmetry from $P6_3$/mmc to $Cmc2_1$. The proton-ordered phase was designated as ice XI. Our experiments are always governed by the Deborah number D [23], which is defined as the ratio of the relaxation time and observation time. For a system D«1, we can observe the whole shape of heat capacity anomaly associated with the possible ordering transition that is determined by intermolecular interaction and cooperative nature of the interaction. For a system D«1, however, we will miss a part or full of the relevant thermodynamic quantity owing to our limited experimental time. The relaxation time is determined by disordered structure and barrier height hindering the rearrangement of the structure. A particular impurity doped into the system will modify drastically the dynamics of the rearrangement and reduce the relaxation time of the system as a whole [24].

A particular kind of dopant acted on frozen-in disordered system as catalyst for releasing the immobilized state and recovering the equilibrium state in our observation time. In relation to this fact, one might raise an inquiry ‘What kind of physical or chemical impurity will release the frozen-in state of the liquid?’. If a particular dopant be discovered luckily for this purpose, we will be blessed to observe in reality ‘What will happen at the Kauzmann temperature of a liquid?’. As a matter of fact, it is not easy for us to imagine some disordered solids without any configurational entropy, designated as an ‘ideal glass’.

It is worth mentioning here an ideal-like behavior of amorphous water. In spite of its simple molecular structure, a wide variety of state of aggregation of water molecules has been observed hitherto. At least thirteen crystalline forms of ice designated as I_h, I_c, II, III, IV, ···, XI, as well as vapor-deposited amorphous ice have been found to exist under atmospheric and high pressures as of 1982. Then Mishima *et al.* have developed pressure-induced amorphization for ice. They prepared high-density amorphous (HDA) and low-density amorphous (LDA) ices by pressurizing I_h or I_c at 77 K up to 1.6 GPa [25]. Both the amorphous ices changed each other by an apparent first-order transition. The phenomenon designated as ‘polyamorphism’ has opened a new realm in the science of amorphous solids. Particularly interesting is the properties of LDA ice. It is becoming increasingly clear that LDA ice is of extraordinary character among amorphous solids. First, the LDA ice did not show boson peaks that were widely observed in glass-forming liquids [26]. Secondly, LDA showed a dispersion relation for vibrational modes that was similar to ice I_c crystal, as revealed by X-ray scattering [27]. Thirdly, LDA ice had a thermal conductivity that increased with falling temperature like a crystal, showing that heat-carrying phonons are not scattered at low temperatures [28]. It is interesting also to see that the thermal conductivity of LDA is unexpectedly larger than that of HDA. It seems likely that in LDA ice we closely approaching an ideal glassy state [29]. It is an embarrassment, however, that it is not certain that a characteristic T_g can be assigned to this almost ideal glass. Recent discovery of very high-density amorphous (VHDA) ice makes the situation more complex [30]. Further works with novel idea is highly encouraged for an improved understanding of this important subject.

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