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# Effect of pressure on thermal conductivity and pressure collapse of ice in a polymer-hydrogel and kinetic unfreezing at 1 GPa

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We report a study of aqueous solutions of poly(vinylalcohol) and its hydrogel by thermal conductivity,  $\kappa$ , and specific heat measurements. In particular, we investigate (i) the changes in the solution and the hydrogel at 0.1 MPa observed in the 350–90 K range and of the frozen hydrogel at 130 K observed in the range from 0.1 MPa to 1.3 GPa, and (ii) the nature of the pressure collapse of ice in the frozen hydrogel and kinetic unfreezing on heating of its high density water at 1 GPa. The water component of the polymer solution on cooling either first phase separates and then freezes to hexagonal ice or freezes without phase separation and the dispersed polymer chains freeze-concentrate in nanoscopic and microscopic regions of the grain boundaries and grain junctions of the ice crystals in the frozen state of water in the hydrogel. The change in  $\kappa$  with temperature at 1 bar is reversible with some hysteresis, but not reversible with pressure after compression to 0.8 GPa at 130 K. At high pressures the crystallized state collapses showing features of  $\kappa$  and specific heat characteristic of formation of high density amorphous solid water. The pressure of structural collapse is 0.08 GPa higher than that of ice at 130 K. The slowly formed collapsed state shows kinetic unfreezing or glass–liquid transition temperature at 140 K for a time scale of 1 s. Comparison with the change in the properties observed for ice shows that  $\kappa$  decreases when the polymer is added. © 2011 American Institute of Physics. [doi:10.1063/1.3568817]

## I. INTRODUCTION

Interaction of water in solutions and gels of natural organic materials, especially proteins, is hydrophilic *via* hydrogen bond interactions, as well as hydrophobic. Similar interactions occur in solutions and gels of synthetic polymers. Most gelled states, such as those of proteins, cosmetics and medicines, and of coatings used for preservation of foods, are obtained usually by keeping an aqueous solution of the gel-forming material for several hours in the temperature range of 275–280 K. In addition to this method, mechanically stronger gels of synthetic polymers are made by cryogenic treatment of the solution. For example, it has been reported since the 1970s that the procedure of freezing some homogenous polymer solutions by rapid cooling to low temperatures, storing for a definite time, and finally defrosting produces gels with improved properties over those produced by the usual methods. Their elastic modulus is much higher, and they are mechanically more stable over a broad range of temperature while retaining their rubberlike elasticity. These properties improve when the material is subjected to repeated freeze-thaw cycles. Poly(vinyl alcohol) or PVA hydrogels have been particularly studied for the purpose. In a recent paper on studies of the kinetics of gelation of PVA solutions, Auriemma *et al.*<sup>1</sup> provided a review of studies of the aqueous PVA gels. They used time-resolved small angle neutron scattering (SANS), which can reveal changes occurring over 1–100 nm

scale, and found that the ice crystals matrix formed on freezing of the solution contains (unfrozen) liquid microphase. In this microphase, PVA crystallizes slowly according to the first-order kinetics initially and then a much slower kinetics. For concentrations of PVA higher than the critical value, crystallization of PVA is responsible for the formation of mechanically strong physical gels on defrosting. They considered that gel formation, after crystallization of water at  $T < 273$  K, may involve two processes, crystallization of PVA due to eutecticlike behavior and spinodal decomposition of the liquid phase. They indicated that crystallization of water at  $T < 263$  K produces fine ice crystals. This is also the case when deeply supercooled water crystallizes. It is also known that extremely slow crystallization of materials in gels produces unusual crystal microstructures, and more recently nanocrystals have been prepared in this manner.<sup>2</sup>

In contrast to the usual interest in the changes that occur in the polymer's behavior and in its microstructure that lead to the mechanical strengthening of the hydrogel,<sup>1,3–5</sup> we are interested in transformation by structural collapse of nanometer size and larger crystals of ice by application of pressure in the PVA gel. It is known that ice/water melting–freezing temperature is greatly reduced in nanoconfinement and deeply supercooled water at low viscosity crystallizes to fine crystals. Auriemma *et al.*<sup>1</sup> also wrote that crystallization of water in PVA solution is induced at  $T < 263$  K on cooling and it produces fine crystals of ice. Their findings are reminiscent of the freeze-concentration of aqueous solutions in which the impurities aggregate at grain boundaries, as occurs, for example, on seasonal freezing of sea ice, but, owing to their high

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solubility, salts do not readily crystallize in the intergranular solution.

Johari and co-workers studied the nanoconfined states of water and ice in the pores of poly(HEMA) hydrogels<sup>6–10</sup> by using calorimetry, dielectric spectroscopy, and diffraction measurements, and in the pores of silica<sup>11–14</sup> by calorimetry, and discussed the various interpretations of the state of nanoconfined water. In these matrices, the behavior is affected by the H<sub>2</sub>O's interactions with the hydroxyl groups in poly(HEMA) and the siloxane groups in silica pores. Pressure-induced collapse of ice crystals of different sizes to a higher density, apparently amorphous structure is also of significant interest, and ice crystals in gels provide a simpler method for investigating the mechanism of this collapse. In earlier studies, we used both the thermal conductivity,  $\kappa$ , and dielectric properties to investigate the collapse of hexagonal and cubic ices in both pure state<sup>15,16</sup> and impure state<sup>17</sup> and of ice clathrates<sup>18,19</sup> by using the same procedure, and further investigated the nature of the resulting high density amorphous (HDA) solid water by subjecting it to temperature cycles and pressure cycles. Here we report a study of such a collapse of the microcrystalline ice<sup>1</sup> produced by crystallization of aqueous PVA solution. We use the same two concentrations of solutions as in the study of Auriemma *et al.*<sup>1</sup> at 1 bar (0.1 MPa) pressure and investigate the properties of the 10% solution in detail at high pressures. However, our protocol of heating, cooling, and annealing is suited to high pressure measurements. It is known that different protocols yield hydrogels of varying properties, and some of the findings have been debated; the physical mechanism of freeze-concentration of the PVA solution in the frozen state of hydrogel and the strengthening of the gel by freezing and thawing processes are certain. Here, we investigate also the effects of polymer–water interactions on the pressure of structural collapse of frozen ice containing freeze-concentrated solution in the glassy state and the properties of the collapsed state of ice. This first study of thermal conductivity of hydrogels under pressure additionally yields significant information on the phonon scattering effects of continuously evolving multiphase systems. In its practical aspects, heat transport in gels is important for engineering analysis and design for food processing, and attempts have been made to model the heat transport of (protein) hydrogels containing air bubbles.

## II. EXPERIMENTAL METHODS

Poly(vinyl alcohol) or PVA of molecular weight specified as 85 000–124 000 was purchased from Sigma-Aldrich. Homogeneous solutions of PVA were prepared by vigorous stirring 5 and 10 wt. % PVA in water (W 3500 from Sigma Aldrich) under reflux at  $\sim 96^\circ\text{C}$  for 30 min.

Thermal conductivity  $\kappa$  and heat capacity per unit volume  $\rho c_p$  of the samples were measured by the hot-wire technique, which has previously been described in detail.<sup>20,21</sup> For the experiments at 1 bar, we used a 0.3 mm in diameter and  $\sim 70$  mm long Ni wire as hot wire. It was suspended in a holder made of PMMA and placed in a sample tube made of poly(oxymethylene) which was fitted into an aluminum cylinder equipped with heater. The assembly was cooled by either

a freezer or using liquid nitrogen. For the high pressure experiments, the hot wire was a 0.3 mm diameter 40 mm long Ni wire, which was placed horizontally in the shape of a ring of constant radius to best use the limited space available within a Teflon sample cell. The Teflon cell is closely fitted inside a piston-cylinder-type apparatus of 45 mm internal diameter and the whole assembly is transferred to a hydraulic press that supplies the load. The temperature of the sample was varied by heating or cooling the whole vessel by means of a built-in refrigerator, which uses a closed helium gas cycle.<sup>22</sup> (In our procedure, it is normally required that a solid sample be kept under slight pressure so that thermal contact of the hot wire with the solid is maintained during a set of measurements. This is done even when volume expansion on freezing of water in a sealed container raises the pressure of the content.) Pressure was determined from the load/area and corrected for friction, which had been determined in an *in situ* experiment using the pressure dependence of the resistance of a manganin wire. The temperature was measured by a chromel-alumel thermocouple, which had been previously calibrated against a commercially available silicon diode thermometer. The temperature reported here is that of the sample plus the average of the hot-wire temperature rise during the heat pulse.

The hot wire, surrounded by the sample, was heated by a 1.4 s long pulse of nominally constant power, and its electrical resistance was measured as a function of time, i.e., the wire acted as both heater and sensor for the temperature rise, which was calculated by using the relation between its resistance and temperature. The analytical solution for the temperature rise with time was fitted to the data points for the hot-wire temperature rise, thereby yielding  $\kappa$  and  $\rho c_p$  with estimated inaccuracies of  $\pm 2\%$  and  $\pm 5\%$ , respectively, and standard deviation an order of magnitude smaller.

When errors in the  $\kappa$  measurements during cooling or depressurizing systematically increased, it indicated poor thermal contact of hot wire with the sample that worsened on cooling or pressure decrease. However, there was no such indication in the set of data obtained at 1 bar pressure here. A large systematic deviation of the fitted analytical solution from the measured temperature rise also appeared when an exothermic or endothermic transformation of the sample occurred. In this case, the real-time fitting routine sometime failed and automatically terminated the data collection. This led us to investigate the nature of the transformation itself.

In the vicinity of a glass–liquid transition,  $\kappa$  often shows a broad peak, i.e., change in  $d\kappa/dT$ , typically from being weakly positive at  $T$  below the glass–liquid transition temperature  $T_g$  to weakly negative at  $T > T_g$ , which is due to the increase in the thermal expansivity that occurs at  $T_g$ .<sup>23,24</sup> This has been observed in our study of polymers,<sup>24</sup> in studies of polymerization kinetics,<sup>25</sup> and by several others.<sup>23,26</sup> Its discussion has appeared also in Ref. 25. Moreover,  $\rho c_p$  increases in the glass to liquid transition range because  $c_p$  increases in a sigmoid shape manner on heating a glass through this range, and these features depend upon the time scale used for the measurement. This time scale is set by the heating pulse time of the hot wire, which is 1 s. Thus, the kinetic unfreezing temperature on heating the glassy state and the kinetic freezing temperature

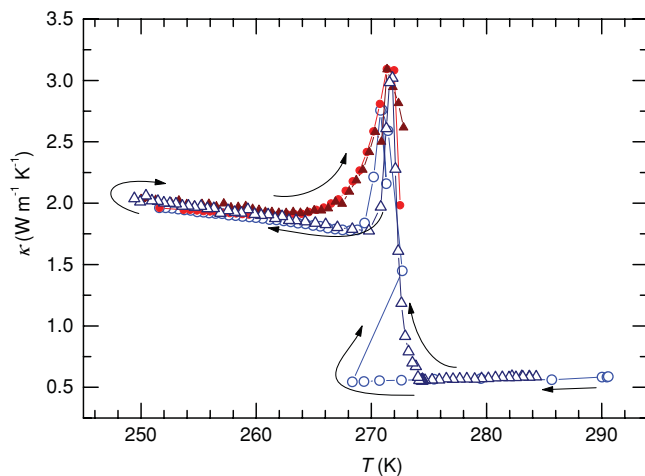


FIG. 1. Thermal conductivity of a 5 wt. % PVA–water solution at 1 bar during first cooling (open circles, blue) from 290 to  $\sim 250$  K and reheating to 273 K (filled circles, red), and second cooling (open triangles, navy) from 284 K and subsequent reheating (filled triangles, wine). The average cooling and heating rates were  $0.3 \text{ K min}^{-1}$  and  $0.2 \text{ K min}^{-1}$  and the waiting time for the sample during crystallization at  $\sim 273$  K were about 10 and 30 min, respectively. The sample was initially a homogeneous solution, but after crystallization on cooling and heating to room temperature it had transformed to a hydrogel.

on cooling the melt through the glass–liquid range correspond to 1 s time scale. In contrast, in calorimetric studies of the glass–liquid transition, these features and  $T_g$  itself depend on the heating rate as well as the rate of cooling to form glass.

### III. RESULTS

We first performed a preliminary investigation of the 5 and 10 wt. % PVA in water solutions at 1 bar pressure by measuring its  $\kappa$  during cooling and heating. The results for the 5 wt. % sample are plotted against the temperature in Fig. 1 whose caption gives the protocols for heating and cooling. This provides us the characteristic features of phonon properties on transformation between the homogenous solution (sol) and gel at 1 bar. In Fig. 1,  $\kappa$  of the solution is  $0.584 \text{ W m}^{-1} \text{ K}^{-1}$  at 290 K, and on cooling at  $18 \text{ K h}^{-1}$  rate it decreased to  $0.544 \text{ W m}^{-1} \text{ K}^{-1}$  at 268 K indicating partly the lowering of the freezing point of water to 268 K, but mostly the supercooling of the sol. At 268 K, the temperature of the sample increased to 273.3 K as water began to crystallize rapidly and the apparent  $\kappa$  increased reaching an anomalously high value. (The increase is an artifact of the endothermic effect when crystals melt and severely retard the heating of the probe.<sup>27</sup>) On cooling to 269 K,  $\kappa$  decreases progressively more slowly and finally it increases with decreasing temperature and becomes  $1.97 \text{ W m}^{-1} \text{ K}^{-1}$  at 251 K.

The sample was then heated at  $12 \text{ K h}^{-1}$  rate and at  $\sim 264$  K; its  $\kappa$  began to deviate from the values measured on cooling. It became progressively higher than the  $\kappa$  measured on the cooling path, and accidental failure of the fitting routine prevented measurements beyond 273 K. As in the ambient pressure studies of Auriemma *et al.*,<sup>1</sup> the sample was

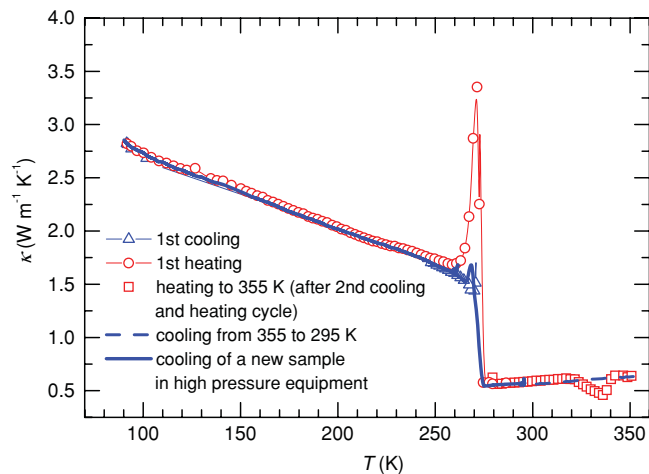


FIG. 2. Thermal conductivity of a 10 wt. % PVA–water solution at 1 bar: (triangles, blue) data on slow cooling at  $0.1 \text{ K min}^{-1}$  rate from 270 to 245 K and then rapid cooling at  $9 \text{ K min}^{-1}$  rate to 90 K, (circles, red) reheating to 273 at a rate  $0.35 \text{ K min}^{-1}$ , where the measurements failed. A second similar cooling and heating cycle, not shown, was done before heating up to 355 K at  $0.15 \text{ K min}^{-1}$  rate (squares, red) and cooling to 293 K at  $0.1 \text{ K min}^{-1}$  rate (dashed blue line). Thermal conductivity of a new sample of 10 wt. % PVA–water solution as measured on cooling at a rate of  $0.4 \text{ K min}^{-1}$  shown by blue full line. The sample was at 1 bar (0.1 MPa) pressure on cooling until 258 K, where it was annealed for 2 h. The pressure was then raised to 0.03 GPa, and further raised to 0.07 GPa in the range on cooling from 190 to 160 K range. The pressure was increased to ascertain that sample remained in contact with the probe wire. This increase has only a very small effect on  $\kappa$ .

initially a free flowing solution at 298 K, which crystallized on cooling. After heating back to 298 K it was found to be a gel, thus indicating a transformation of the sol to gel state with a significant hysteresis. On subsequent cooling,  $\kappa$  is the same as on the first cooling path in Fig. 1 except that the sample did not supercool and  $\kappa$  instead increased slowly at about 274 K. On the subsequent second heating,  $\kappa$  is the same as on the first heating path.

In order to enhance the effect of the polymer on  $\kappa$  and on the sol–gel transformation itself, we doubled the amount of PVA to 10 wt. %, and studied how  $\kappa$  changes during the cooling of this solution and subsequent heating. To establish a protocol for high pressure measurements at low temperatures, we also studied  $\kappa$  of the sample by cooling to 90 K. The plots of  $\kappa$  against  $T$  are shown in Fig. 2. To allow longer time for the transformation, the sample in this case was cooled at  $0.1 \text{ K min}^{-1}$  rate from room temperature to 245 K, and then rapidly cooled at  $9 \text{ K min}^{-1}$  rate to 90 K. This increased  $\kappa$  of the frozen sample from  $1.5 \text{ W m}^{-1} \text{ K}^{-1}$  at 270 K to  $2.8 \text{ W m}^{-1} \text{ K}^{-1}$  at 90 K. The sample was subsequently heated to 273 K at  $0.35 \text{ K min}^{-1}$  rate, where the fitting routine failed again. In a repeated cooling and heating cycle, the sample did not supercool, but outside the transition range  $\kappa$  retraced the data in the first cycle. After the completion of the second temperature cycle, the sample was further heated to 355 K at  $0.15 \text{ K min}^{-1}$  rate. It was finally cooled to 293 K at  $0.1 \text{ K min}^{-1}$  rate. As for the 5 wt. % sample, the data obtained on heating showed an increasing deviation from those obtained on cooling with onset at about 264 K. This deviation was accompanied by an increased error in the data on

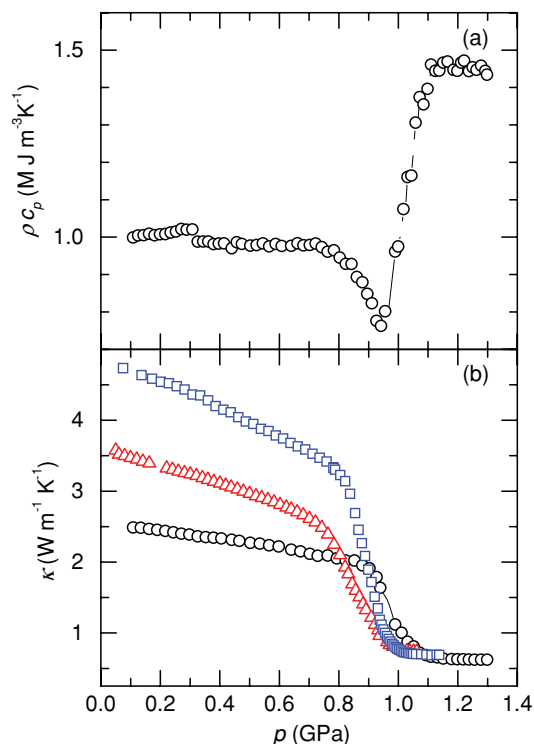


FIG. 3. (a) Heat capacity per unit volume and (b) thermal conductivity of a 10 wt. % PVA–water solution on isothermal pressurization at 130 K (circles, black). Similar studies of ice had shown that the features observed in thermal conductivity are due to collapse of the ice structure. For comparison the data for ice Ih (squares, blue) (Ref. 16) and ice Ic (triangles, red) (Ref. 15) are also plotted in (b).

heating, which was noticed at  $\sim 263$  K. (The error is derived from the difference between the fitted analytical function and the measured values for the temperature rise of the wire probe, as described in Sec. II). At about 280 K, when  $\kappa$  was  $0.561 \text{ W m}^{-1} \text{ K}^{-1}$ , the error had decreased to its normal value. On further heating,  $\kappa$  first increased to  $0.615 \text{ W m}^{-1} \text{ K}^{-1}$  at 318 K and then decreased to  $0.459 \text{ W m}^{-1} \text{ K}^{-1}$  at 336 K before abruptly increasing to  $0.643 \text{ W m}^{-1} \text{ K}^{-1}$  at 342 K. Also in the 336–342 K temperature range, the error increased to anomalously large values. On subsequent cooling,  $\kappa$  decreased in parallel with the results on heating outside the 336–342 K range, but was about 5% lower.

To examine the reproducibility of the data and the effect of pressure, a new sample of 10 wt. % PVA in water was made and studied during cooling from 295 to 90 K. After initially freezing at 1 bar and 273 K, the sample was annealed at  $258 \pm 2$  K for  $\sim 2$  h. The pressure was thereafter raised to 0.03 GPa, and then further to 0.07 GPa slowly on cooling (see Fig. 2 for details). The  $\kappa$  values of the new sample, which are plotted in Fig. 2, agree with the values of the previous sample measured on heating at 1 bar to within 1%.

The crystallized sample was heated at  $\sim 0.4 \text{ K min}^{-1}$  from 90 to 130 K and maintained at 130 K. The pressure,  $p$ , was increased at  $\sim 0.15 \text{ GPa h}^{-1}$  rate to 1.3 GPa and its  $\kappa$  and  $\rho c_p$  were simultaneously measured. The results are plotted against  $p$  in Fig. 3. For comparison, we have also plotted the corresponding values of  $\kappa$  of ice taken from our earlier studies.<sup>15,16</sup> The pressure was then decreased to 1 GPa, the

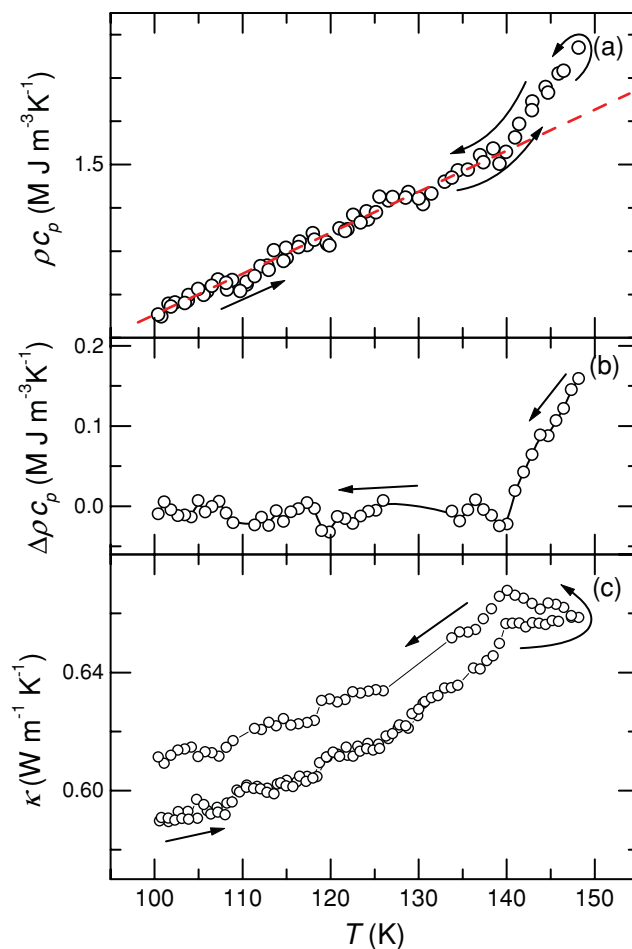


FIG. 4. (a) Heat capacity per unit volume, (b) excess heat capacity per unit volume, and (c) thermal conductivity of the pressure-collapsed state of 10 wt. % PVA–water solution at 1 GPa plotted against the temperature. The arrows indicate heating from 90 to 148 K at  $0.1 \text{ K min}^{-1}$  rate, and subsequent cooling to 100 K at  $0.25 \text{ K min}^{-1}$  rate at 1 GPa. The dashed line describes the data of the frozen state below 140 K (for a time scale of 1 s), which were subtracted to obtain the excess values shown in (b).

sample kept at that pressure, and its  $\rho c_p$  and  $\kappa$  were measured on heating from 90 to 148 K at  $6 \text{ K h}^{-1}$  rate and thereafter measured on cooling to 148 K at  $15 \text{ K h}^{-1}$  rate. The results are plotted against  $T$  in Fig. 4.

Finally, in order to study the transformation of the collapsed state on heating the sample at  $p$  near 1 bar, the sample kept in the 90–100 K range was depressurized at  $0.1 \text{ GPa h}^{-1}$  rate from 1 to 0.06 GPa. It was temperature cycled between 90 and 125 K and then continuously heated (see Fig. 5 for details). At about 137 K, an exothermic transformation occurred which raised the temperature to 175 K and  $\kappa$  increased abruptly. After the heat had dissipated to the surrounding vessel,  $\kappa$  was  $1.7 \text{ W m}^{-1} \text{ K}^{-1}$  at 141 K. On further heating from 141 to 162 K,  $\kappa$  decreased slightly. It then increased slowly on heating to 190 K and thereafter decreased slightly. At 257 K,  $\kappa$  increased anomalously by a large amount just before fracture of the wire probe aborted this set of experiments.

For reasons described in Sec. I, our experimental protocol differs from that in previous studies,<sup>1,3</sup> and it is worth

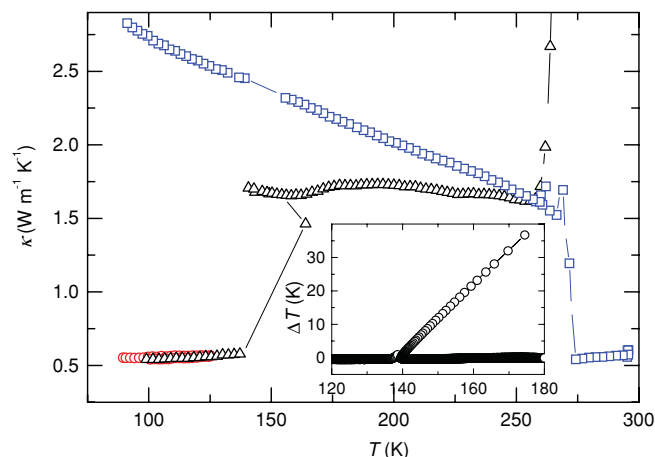


FIG. 5. Thermal conductivity of a collapsed 10 wt. % PVA–water solution at 0.06 GPa on heating. The temperature of the sample was first cycled from 90 to 125 K and then to 100 K (circles, red). It was then continuously heated to 260 K (triangles, black), initially at  $0.3 \text{ K min}^{-1}$  rate, which decreased to  $0.05 \text{ K min}^{-1}$  near 260 K where the sample probe broke when the sample phase transformed. The thermal conductivity of an as-made 10 wt. % PVA–water solution measured on cooling at a rate of  $0.4 \text{ K min}^{-1}$  (squares, blue) is shown for comparison. The sample was at 1 bar (0.1 MPa) pressure on cooling until 260 K. It was then raised to 0.03 GPa, and further raised to 0.07 GPa in the range on cooling from 190 to 160 K range. The pressure was increased to ascertain that sample remained in contact with the probe wire. This increase has only a very small effect on  $\kappa$ . The inset shows the rise in the sample temperature in the 140–180 K range calculated by subtracting a baseline. In this temperature range  $\kappa$  increases by a factor of 3, as seen in the plot (triangles, black) in the main figure.

noting this difference. Briefly, the study of Auriemma *et al.*<sup>1</sup> was aimed at obtaining simultaneous information on the gelation mechanism and the kinetics of formation of PVA aggregates responsible for the development of a mechanically strong, stable gel network, and it supported a model (Fig. 3, Ref. 1) for the bicontinuous structure of PVA hydrogels. In their protocol for studying the gelation kinetics, aqueous 10 wt. % PVA solution was cooled rapidly to 260 K, and then the time evolution of the microstructure was studied. They found<sup>1</sup> that the most significant change occurred within  $\sim 1 \text{ h}$  after cooling the sample, and after that the kinetics significantly slowed down. Crystallization of water on cooling the PVA solution at  $T < 263 \text{ K}$  produced fine crystals of ice,<sup>1</sup> and subsequent thawing melted the ice, and a macroscopic gel formed. It is possible that a similar state was formed in our study when the solution cooled from 298 K crystallized and annealing of the crystallized state for 2 h at  $258 \pm 2 \text{ K}$  allowed the fine crystals of ice to grow. As in their interpretation,<sup>1</sup> this established the essential parts of the gel network before or after annealing. But the microstructure of the frozen state obtained here would be different from the frozen state formed in their<sup>1</sup> study as well as the one formed in those studies in which change in mechanical properties on freeze-thaw cycling of the gel was investigated.<sup>3</sup> To maintain distinction, here we use the term frozen-hydrogel. On further cooling, we do not expect a significant change in the network structure of the frozen-hydrogel. Only a change in the state of hydrogen bonds and their population is likely.

## IV. DISCUSSION

### A. Thermal conductivity of the hydrogel, gel–sol transition, and reversible shrinkage

PVA hydrogel is regarded as temperature sensitive gel with gel–sol transition occurring in the 328–363 K range<sup>4</sup> and a “critical transition temperature” of  $\sim 310 \text{ K}$  for discharging of water.<sup>5</sup> On heating to  $T > 310 \text{ K}$ , it loses water and shrinks, and on cooling below 275 K it reabsorbs water and dilates.<sup>5</sup> The plot of its  $\kappa$  against  $T$ , given in Fig. 2, shows a transition in the 318–342 K range, which agrees with the transition range observed by Hatakeyema *et al.*<sup>4</sup> using differential scanning calorimetry (DSC). The DSC scans in their Fig. 2 for a 10 wt. % hydrogel show that after two freeze-thaw cycles the sample began to transform at  $T$  just below 322 K, and complete transition occurred when  $T$  exceeded 345 K. Its occurrence over a  $\sim 25 \text{ K}$  range produces a mixture of at least two phases, one a compositionally different hydrogel because of discharging of water and the other a water–polymer solution. The sluggish transition occurring over a broad temperature range had a latent heat of less than  $1 \text{ J g}^{-1}$ ,<sup>4</sup> which is insufficient to cause  $\kappa$  to increase anomalously as, e.g., occurred on the melting of ice. On further heating above the transition range, the sample should become progressively more homogeneous and finally reach a state similar to that of the as-made solution.

On continuous heating at 1 bar pressure,  $\kappa$  first decreases during this transition at  $\sim 318 \text{ K}$  as seen in Fig. 2, and then increases to the original value at  $\sim 342 \text{ K}$  indicating that the state approaches that of the as-made solution. A reverse transition was not observed on cooling, which agrees with the behavior of the as-made PVA–H<sub>2</sub>O solution, which did not become a gel by keeping at 298 K for several months. In a practical context, we point out that the transition temperature of about 318 K is close to the human body temperature and PVA hydrogel is regarded as biomaterial for articular cartilage. This would make the observation of medical significance, as it indicates that the hydrogel would slowly degrade with temperature rise and recovery of the gel would require freeze-thaw cycles.

### B. Thermal conductivity of the hydrogel, state of water, and crystallization

Both 5 and 10 wt. % hydrogels show an increase in  $\kappa$  on cooling through the 274–270 K temperature range, which is due to crystallization of the water in the hydrogel. On first cooling of the 5 wt. % sample, there is a supercooling by  $\sim 5 \text{ K}$  as seen in Fig. 1. This also occurred for the 10 wt. % solution in the identical setup, but not in the high pressure cell. The transformation is reversible, but not retraceable in the  $\kappa$ – $T$  path. The melting of ice begins at a lower temperature, a phenomenon known as premelting. It is observed when the crystal grain size in a polycrystalline material is small and melting occurs at the grain junctions and grain boundaries. The latent heat (absorbed) on premelting appears as a slow rise of  $C_p$  producing an endothermic peak.<sup>28,29</sup> Simultaneously, the latent heat increases the error in measuring  $\kappa$ , whose value increases as an artifact.<sup>27</sup> Hence, the

transition on heating appears over a 4 K wider temperature range on heating (263–273 K) than on cooling (273–269 K).

It has been observed that nm-size crystals of PVA are dispersed in the hydrogel.<sup>30</sup> These nanocrystals act as knots, or nodes, that link the randomly oriented polymer chains leading to a loosely packed network structure. Their spatial distribution is random but uniform, which gives a hydrogel its homogeneity. In this way, polymer network becomes the continuous phase and the liquid the discontinuous phase. At 290 K, the 10 wt. % hydrogel has a marginally lower  $\kappa$  of  $0.574 \text{ W m}^{-1} \text{ K}^{-1}$  than the 5 wt. % hydrogel whose  $\kappa$  is  $0.587 \text{ W m}^{-1} \text{ K}^{-1}$ . The values are 3% and 0.8% less than  $\kappa$  of  $0.592 \text{ W m}^{-1} \text{ K}^{-1}$  for pure water at 290 K.<sup>31</sup> Still, like  $\kappa$  of pure water, they decrease on cooling. This indicates that hydrogen bond interactions that stabilize the shape of a gel and raise its elastic modulus have marginally small effect on  $\kappa$ .

After the samples have crystallized,  $\kappa$  increases to 1.60 and  $1.88 \text{ W m}^{-1} \text{ K}^{-1}$  at 260 K, respectively, for the 10 and 5 wt. % initial-composition hydrogel. It increases on cooling like that of ice and other crystalline solids. In the temperature range of 250–260 K,  $(d\kappa/dT)_p$  is relatively higher for the 5 wt. % hydrogel that contains a higher amount of ice, and therefore it may be seen as  $\kappa$  value for the composite of partially crystallized PVA and ice, as analyzed for other polymer composites.<sup>32</sup>

There is no doubt that  $\kappa$  of the frozen hydrogel is dominated by the amount of ice present. We attempted to determine whether or not  $\kappa$  of the ice mixtures can be described by the effective medium approximation model<sup>33</sup> or the Maxwell model<sup>34</sup> used earlier for a composite of AgCl particles in polyethylene.<sup>35</sup> In doing so we assumed that all water transforms to ice Ih and that ice Ih and PVA are mechanically separable solids, and then used  $\kappa$  of PVA of unknown molecular weight from Ref. 36 and that of ice Ih from Ref. 21. We found that the calculated value of  $\kappa$  of the crystallized PVA hydrogel was much too large at all temperatures. We also varied the fraction of ice in the model calculations to determine if a lower fraction of ice would make the models agree with the data. The  $\kappa$  values at high temperatures could be matched by assuming  $\sim 78\%$  ice in the frozen 10 wt. % PVA hydrogel, but the values were still too large at low temperatures, i.e., the  $T$  dependence of the models differed from the experimental data.

The crystallized PVA hydrogel consists of a mixture of ice and unfrozen solution of higher PVA concentration than the original solution. Yokoyama *et al.*<sup>30</sup> have provided an illustration in their Fig. 7 of a model (also appeared as Fig. 3 in Ref. 1) in which there are interconnected chains of PVA through nodes of PVA crystals, and there are large voids formed in this network structure, which contain ice. They wrote, “The model shows that the hydrogel is composed of the following three kinds of phases: water phases or solutions phases with a very low concentration of PVA, which in the frozen gel correspond to the crystal phases of ice; amorphous phases, in which every PVA chain is associated with water; PVA crystal phases, which restrain gross mobility of the amorphous chains.” The PVA chains are mostly segregated in the unfrozen liquid, which is referred to as liquid microphase in which PVA slowly crystallizes. These regions

containing crystallites act to form a network structure of polymer rich regions or swollen polymers. The 10 wt. % crystallized hydrogel is nonuniform due to large regions that form heterogeneities dispersed within the ice matrix. It has been argued that the nonuniform structure of the crystallized hydrogel is due to presence of the unfrozen liquid microphase of 85–90 nm dimensions containing PVA crystallites, as was found from SANS study.<sup>1</sup> It is to be noted that PVA in the microphase at 260 K was found to crystallize for a period of up to 400 min and the Avrami equation was fitted to the data.<sup>1</sup> In our studies, the sample was annealed for only 2 h at 260 K, and then cooled further at  $0.3 \text{ K min}^{-1}$ . As the diffusion coefficient of the PVA chains would rapidly decrease on cooling, it is unlikely that PVA in the microphase here would have crystallized to the same extent as in the samples used for SANS study.<sup>1</sup> Therefore, a significant amount of the microphase containing fewer crystals of PVA in our study would have vitrified on cooling.

Neither a randomly dispersed PVA chain nor the 3–4 nm size PVA crystallites can be accommodated on the lattice sites of an ice structure. Therefore, they would become freeze-concentrated in water at the grain boundaries and grain junctions of polycrystalline ice, similar to the occurrence of freeze-concentration solution in the channels formed by three-grain boundaries and tetrahedral pockets at the four grain junctions that connect these channels in polycrystalline materials.<sup>28</sup> (The freeze-concentrated salt solution on formation of sea ice is a well-known example of this occurrence.) In such a structure, the population (per unit sample volume) of unfrozen liquid microphase of  $\sim 85\text{--}90 \text{ nm}$  dimensions is not known, but the ice crystal size leading to this unfrozen liquid microphase population can be approximately estimated, as given in Refs. 28 and 29. We suggest that the broad melting curve of the frozen hydrogel at 1 bar with onset near 265 K (8 K less than 273 K for pure ice) indicates the effects of premelting at the boundaries of three- and four-grain junctions, which is enhanced by the presence of impurities. Premelting begins at a lower temperature and is more easily observed when the crystal grain size in a polycrystalline material is small. This was observed for polycrystalline samples made by quenching water in liquid nitrogen which contained 1–5  $\mu\text{m}$  diameter ice crystal grains.<sup>29</sup> Wilson *et al.*<sup>37</sup> have already reviewed several aspects of premelting effects. They too noted that Dash and co-workers<sup>38–42</sup> discussed the presence of intergranular water and concluded that if the radius of curvature of the ice grains is 1  $\mu\text{m}$  liquid water can be present down to  $\sim 263 \text{ K}$ . We also note that ice formed in nanopores of silica and other solids shows a melting endotherm that is broadened out on the low temperature side,<sup>43–45</sup> making it difficult to define the onset of bulk melting. The poorly defined onset temperature for melting of ice in 100% filled, 4 nm diameter pores of Vycor glass is  $\sim 245 \text{ K}$  (with a peak at 260 K) in Fig. 4, Ref. 12. As discussed previously,<sup>11,13</sup> hydrogen bond formation with silica also has an important role in thermodynamics of melting in such cases.

In a solid, the phonon mean free path is limited by various scattering processes such as phonon–boundary scattering and phonon–phonon scattering, which determine the magnitude of  $\kappa$  and its variation with  $T$ . Dominance of the latter gives  $\kappa$

$\propto T^{-1}$ , whereas the hydrogel shows significantly weaker temperature dependence for  $\kappa$  ( $n$  between 0 and 1 in  $\kappa \propto T^{-n}$ ). Therefore, we conclude that the nm-size crystallites of PVA and the  $\mu\text{m}$ -size ice crystal grains with intergranular freeze-concentrated solution limit the mean free path of phonons and thus affect both the magnitude and temperature dependence of  $\kappa$ . There may be additional effects arising from a large surface area with a distribution of (grain size dependent) interaction energies, from hydrogen bond interactions between the crystallized PVA and water molecules of the ice matrix.

### C. Change in the heat capacity and thermal conductivity with pressure and collapse of ice

Figure 3(a) shows the change of  $\rho c_p$  on isothermal pressurization at 130 K. The small slope in the 0.1–0.75 GPa range indicates that increase in  $\rho$  on pressurization is mostly compensated by a decreasing  $c_p$ . At  $p > 0.8$  GPa,  $\rho c_p$  first decreases more abruptly and then increases as the hydrogel collapses and densifies. On normal densification without a change in the structure,  $c_p$  decreases and  $\rho$  increases gradually with increase in pressure and the product  $\rho c_p$  does not show both a decrease and an increase. We attribute this feature to the change in the state of the frozen hydrogel on collapse, like that for ice.<sup>16</sup>

The change in  $\kappa$  obtained here on pressurization at 130 K [Fig. 3(b)] shows the same features as reported before for ice<sup>15</sup> and for a mixture of a clathrate hydrate and ice,<sup>17</sup> i.e.,  $\kappa$  decreases initially almost linearly with  $p$  followed by a more abrupt decrease on pressure collapse. Like the collapse of ice, it occurs at  $p$  of  $\sim 1$  GPa, and probably in a  $T$ ,  $p$ , and time dependent manner,<sup>46</sup> to an apparently amorphous state. Both  $\rho c_p$  and  $\kappa$  show complementary features for the structural collapse of the hydrogel, but the collapse is shifted to slightly higher pressures than that for ice.

The plots in Fig. 3(b) also show that at 130 K  $\kappa$  of the crystallized hydrogel decreases more slowly with increasing  $p$  up to 0.8 GPa than for ice Ih and Ic. The  $\text{dln}\kappa/\text{d}p$  values are  $-0.24 \text{ GPa}^{-1}$  for the hydrogel,  $-0.43 \text{ GPa}^{-1}$  for ice Ih, and  $-0.41 \text{ GPa}^{-1}$  for ice Ic. The lower value is attributable to the fact that the hydrogel contains intergranular freeze-concentrated solution resulting from incomplete crystallization of the 95–90% water in its structure and polymer lamellas whose  $\kappa$  is lower than that of the ices and which increases with increasing  $p$ .

As the ice structure begins to collapse under pressure,  $\kappa$  decreases. The onset pressures<sup>47</sup> of this decrease are 0.86 GPa for the hydrogel, 0.78 GPa for ice Ih, and 0.68 GPa for ice Ic.  $\kappa$  decreases to approximately the same value of  $(0.66 \pm 0.03) \text{ W m}^{-1} \text{ K}^{-1}$  at 1.2 GPa and then remains constant on further increase in  $p$  to 1.3 GPa. (Note that in the earlier study of ice Ic,<sup>15</sup> the maximum pressure was 1.05 GPa when  $\kappa$  was  $0.72 \text{ W m}^{-1} \text{ K}^{-1}$  and weakly decreasing.) The remarkable agreement between the  $\kappa$  of the collapsed state in the above-given three states indicates that, at 1.2 GPa,  $\kappa$  of the pressure collapsed state of the frozen hydrogel is not greatly different from that of ice Ih or ice Ic. It should be noted that the freeze-concentrated solution would be in the

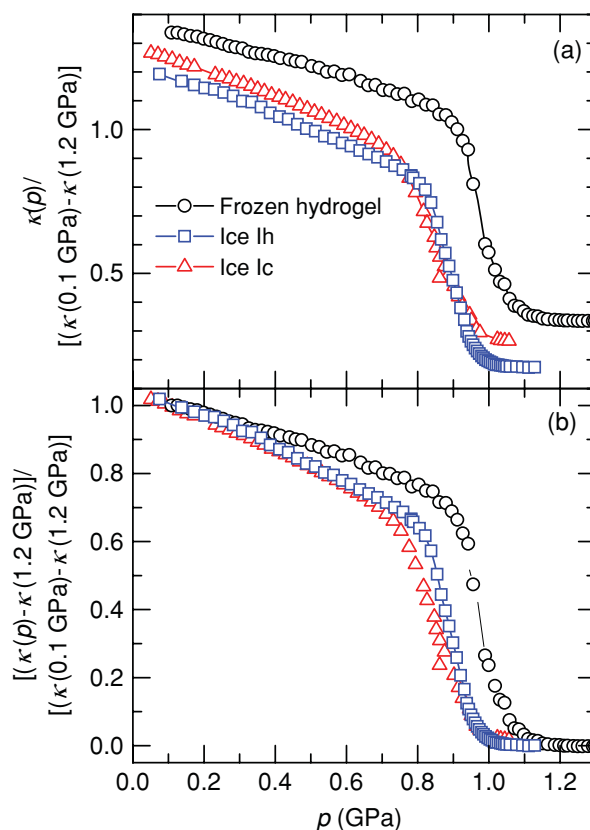


FIG. 6. The normalized value of thermal conductivity of the frozen hydrogen is plotted against the pressure: panel (a) is for  $\kappa(p)/[\kappa(0.1 \text{ GPa}) - \kappa(1.2 \text{ GPa})]$  and panel (b) for  $[\kappa(p) - \kappa(1.2 \text{ GPa})]/[\kappa(0.1 \text{ GPa}) - \kappa(1.2 \text{ GPa})]$ . For the plot in (b) the same  $\kappa$  value was used for the collapsed state of ice Ic (Ref. 15) and ice Ih (Ref. 16). [In the earlier study of ice Ic (Ref. 15) the maximum pressure reached after collapse was 1.05 GPa when  $\kappa$  was  $0.72 \text{ W m}^{-1} \text{ K}^{-1}$  and weakly decreasing. We use 1.2 GPa to normalize the plots at which  $\kappa$  for ice Ih is close to  $0.69 \text{ W m}^{-1} \text{ K}^{-1}$ , and the same value was used for ice Ic.] The plot starts at 0.1 GPa because the actual values were measured at  $\sim 0.1$  GPa and not at 1 bar pressure. The plots show that the collapse occurs more sharply and over a narrower pressure range for the frozen hydrogel than for the ices.

glassy state at 130 K because its  $T_g$  would be higher than  $T_g$  of 136 K for pure water at 1 bar for  $30 \text{ K min}^{-1}$  heating rate.<sup>48</sup> Since  $\kappa$  of the pressure collapsed hydrogel is about the same as that of collapsed ice Ih and Ic, and the collapsed hydrogel contains both pure ice and glassy state of freeze-concentrated solution, we deduce that  $\kappa$  of the freeze-concentrated glassy solution also would not be greatly different from that of collapsed ice Ih or Ic.

If a certain amount of water in the hydrogel did not crystallize and  $\kappa$  of the remaining polymer–water fraction increased with  $p$ , the decrease in  $\kappa$  on pressure collapse would be lesser than the decrease one would observe if all water crystallized. To show that not all water in the hydrogel crystallizes, we have plotted normalized value of  $\kappa$ , as  $\kappa(p)/[\kappa(0.1 \text{ GPa}) - \kappa(1.2 \text{ GPa})]$  in Fig. 6(a). Here decrease in  $\kappa$  for the crystallized hydrogel is less than that of the ices. We also construct the plots for  $[\kappa(p) - \kappa(1.2 \text{ GPa})]/[\kappa(0.1 \text{ GPa}) - \kappa(1.2 \text{ GPa})]$  against  $p$  in Fig. 6(b) by assuming that  $\kappa$  of the collapsed ice Ic is the same as that of ice Ih at 1.2 GPa. The plots show broadening of the inverted sigmoid shape, which

indicates different rates of collapse for the same rate of increase in  $p$  for different ices.

The increase in the onset pressure for collapse of ice in crystallized hydrogel is unexpected, and although it is only  $\sim 0.1$  GPa the increase is beyond our experimental error. A smaller grain size of ice Ih has been found to lower the onset pressure,<sup>49</sup> and therefore the effect of smaller grain size of ice Ih is overcompensated by another effect that is related to the structure of the crystallized hydrogel. We recognize that the crystallized hydrogel consists of three components: (i) nm-size crystallites of PVA, (ii) intergranular, freeze-concentrated solution that contains the polymer chains that link the PVA crystallite nodes to form a crosslinked network of PVA, and (iii) small size crystals of ice Ih. Because of their relatively small population, the PVA crystallite would contribute little to the pressure collapse, and they would not transform. A similar effect was observed for the pure tetrahydrofuran ice clathrate, which contained only two components.<sup>18</sup>

We suggest that the increase in the onset pressure corresponds to the energy required to deform the glassy state of the intergranular freeze-concentrated solution at 130 K and  $p$  near 0.8 GPa. (Note that ice Ih is one of the softer materials and it easily deforms along the basal plane. Also, the work done to plastically deform and fracture a material of high (elastic) shear modulus is relatively high, and therefore it is expected to be more for glassy water containing dispersed polymer chains than for polycrystalline ice Ih.) In order to convert the uniaxial load to hydrostatic pressure on ice Ih crystals, the glassy state of the freeze-concentrated solution that contains a network (of PVA crystallites connected to similar crystallites by linear chains) needs to be deformed, and this would require extra energy to pull the length of the PVA chains between the PVA crystal nodes in directions orthogonal to the direction of the uniaxial stress.

#### D. Effect of temperature and thermal cycling of the collapsed state at 1 GPa

We measured  $\kappa$  of the hydrogel at 1 GPa first during heating from 90 to 148 K at  $6 \text{ K h}^{-1}$  rate and then cooling from 148 K at  $15 \text{ K h}^{-1}$  rate. Its plot against  $T$  in Fig. 4(c) shows hysteresis in the  $\kappa$  values, which indicates occurrence of an irreversible process on heating. A similar hysteresis in density has been observed on temperature cycling of the collapsed state of ice (known as the HDA). It is known that, at a pressure near 1 GPa, HDA irreversibly densifies on heating.<sup>50</sup> Therefore, we interpret that the hysteresis in Fig. 4(c) is a result of irreversible densification, i.e.,  $\kappa$  of the collapsed hydrogel at 1 GPa increases on heating in a broad sigmoid shape manner in the 130–140 K range as its state densifies by relaxation of the structure to a lower energy. On cooling from 148 K, the slope becomes negative and a peak appears at 140 K. The peak or change in the sign of  $d\kappa/dT$  at 140 K is typical for the onset of kinetic-freezing on cooling, as is often observed for a glass transition.<sup>23,24,26</sup> As mentioned earlier here, reversal of the sign of  $d\kappa/dT$  at glass transition is mainly due to the change in the thermal expansivity, as was shown by the finding that  $\kappa$  for isochoric condition, obtained by converting the isobaric

$\kappa$  values, does not show reversal in the sign of  $d\kappa/dT$  (Fig. 4, Ref. 24).

The plot of  $\rho c_p$  of the pressure-collapsed 10 wt. % hydrogel at a fixed pressure of 1 GPa against  $T$  in Fig. 4(a) shows a monotonic increase from 90–140 K, and thereafter an abrupt increase in the slope at 140 K. The increase may be mistaken for the usual increase observed toward the point of inflexion in the constant volume specific heat of the Debye theory, but since the rise in the Debye theory occurs near  $0.1 \theta_D$ , the observed temperature of the  $C_p$  rise would imply  $\theta_D > 1000$  K and a too high characteristic frequency of the collapsed state at 1 GPa. Koza *et al.*<sup>51</sup> have given  $\theta_D$  as 230 K for the collapsed state of ice Ih at 1 bar, which is in good agreement with our calculated value of 270 K at 1 GPa.<sup>52</sup> The increase is more distinct than the broad Debye-type increase in the density of vibrational states, which occurs at  $T$  near 27 K for a Debye temperature of 270 K. Therefore, the increase in  $C_p$  is not due to change in the occupation of the density of states; it is mostly due to change in the number of available configurations. The relaxation induced hysteresis, which is observed in  $\kappa$ , is not detected in the data for  $\rho c_p$ . This is partly due to an intrinsic decrease in  $c_p$  on densification that reduces  $\rho c_p$  by partial cancellation of the increase in  $\rho$  by decrease in  $c_p$ .

The increase in density of the relaxed state of collapsed hydrogel on cooling at 1 GPa would typically be less than 1% in the 100–150 K range. Therefore, the plot of  $\rho c_p$  on cooling is effectively the plot of  $C_p$ , the specific heat per mole. In the plot of  $\rho c_p$  of the collapsed state at 1 GPa against  $T$ , a sigmoid shape increase appears with onset at 140 K. This is a characteristic feature of a glass to liquid transition, which also shows its temperature range and from which  $T_g$  is usually determined.

To show the sigmoid shape change more clearly, we have plotted the difference between the measured  $C_p$  and the linearly extrapolated  $C_p$  from low temperatures in Fig. 4(b). The abrupt increase of  $C_p$  at 140 K indicates that the collapsed hydrogel is in the glassy state at  $T < 140$  K and on heating it undergoes kinetic unfreezing or glass–liquid transition at 140 K for a time scale of  $\sim 1$  s used in this study (see Sec. II). Since these glass–liquid transition features were not observed in the sample prior to the collapse, and since the fraction of the freeze-concentrated solution should be small, the glass–liquid transition likely occurs in the collapsed ice fraction of the sample.

#### E. Recovery of the as-made hydrogel on heating at low pressure

The pressure-collapsed hydrogel was heated at about 0.06 GPa, a pressure needed to maintain thermal contact between the sample and the probe when the temperature was changed, and its  $\kappa$  was measured. The plots in Fig. 5 show a rapid increase in  $\kappa$  beginning at 137 K. This indicates the onset of an exothermic transition at 137 K, which raised the temperature by almost 40 K and simultaneously  $\kappa$  increased abruptly, as is seen in the inset of Fig. 5. This is due to cold crystallization and must involve a rapid transformation of all or a significant part of the collapsed ice of the hydrogel. On further heating,  $\kappa$  becomes progressively closer to the  $\kappa$  value

of the as-made frozen hydrogel, and the data coincide just before the melting indicated by the anomalous increase in  $\kappa$  at  $T$  of about 258 K.<sup>27</sup> The close agreement in  $\kappa$  suggests that the state of the hydrogel approaches that of the as-made frozen hydrogel at 258 K. The abrupt crystallization, which raised the temperature at 137 K, occurs in the range where crystallization to ice Ic is expected, but the manner of the abrupt change differs from that typically observed for the collapsed state of ice.

Experiments have shown that on heating the collapsed ices at a fixed pressure below  $\sim 0.07$  GPa the collapsed state of pure ice first transforms to the low density amorphous ice and finally to ice Ic.<sup>53,54</sup> At a pressures above 0.07 GPa,<sup>54</sup> it transforms directly from the collapsed state to a crystalline ice, which is ice Ic at  $p$  near 0.07 GPa (Ref. 54) and a mixture of, e.g., ice IX and ice Ih at 0.2 GPa.<sup>55</sup> Transformation of collapsed ice to ice Ic is sluggish and starts at about 130 K and reaches completion near  $T$  of 150 K.<sup>54</sup> Due to the sluggishness of the exothermic transformation, there is no abrupt temperature rise. On the basis of these findings and the significant increase of  $\kappa$  seen in Fig. 5, we attribute the transition at 137 K to rapid crystallization to mainly ice Ic. It may be that as for the bulk ice samples, ice Ic transforms gradually to ice Ih on further heating and the two ices coexist in a wide temperature range. As transformation to ice Ih increases  $\kappa$ , the gradual increase in  $\kappa$  on heating to the melting temperature may be attributed to slow transformation to ice Ih and the crystal grain growth. The dispersed polymer lamellas as well as the thermal history of the collapsed state may affect kinetics as well as transition temperatures, thus causing the crystallization kinetics to differ from that of the collapsed ices.

## V. CONCLUSIONS

Ice formed in a loosely packed matrix of the partially crystallized poly(vinyl alcohol) collapses at a slightly higher pressure than pure ice. This is attributed to the extra energy required to deform the regions of intergranular glassy water containing dissolved polymer chains before the pressure could be transferred to crystalline ice. Interaction of the OH groups of the polymer chains *via* hydrogen bonding with water may have a further effect on the pressure of structural collapse.

Thermal conductivities of the 5 and 10 wt. % PVA hydrogel are marginally lower (1% and 3% at 290 K) than that of pure water. On freezing the hydrogel,  $\kappa$  increases by nearly a factor of 3.5. Addition of a gel-forming polymer decreases  $\kappa$  of the frozen state relative to that of pure ice. However, the frozen hydrogel behaves like crystalline ice in as much as its thermal conductivity increases on cooling and decreases on pressurization. The fractional increase in thermal conductivity on cooling is less than that observed for cubic and hexagonal ices. The fractional decrease of  $\kappa$  on pressurization is also less than that of the pure ices.

On slowly heating at 1 GPa,  $\kappa$  of the pressure-collapsed hydrogel increases with temperature in a sigmoid shape manner. On cooling from 148 K,  $\kappa$  first increases and then de-

creases showing a peak at 140 K. The peak (i.e., change in the sign of  $d\kappa/dT$ ) typically appears at the onset of kinetic freezing on liquid to glass transition.<sup>23,24,26</sup> Slowly heating and cooling at 1 GPa converts the collapsed hydrogel to an amorphous solid, whose specific heat and thermal conductivity show the characteristic feature of glass transition at 140 K for a time scale of 1 s.

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