

Experimentally proven liquid-liquid critical point of dilute glycerol-water solution at 150 K

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The experimental and theoretical studies of supercooled liquid water strongly suggest that the two liquid waters and their liquid-liquid critical point (LLCP) exist at low temperature. However, the decisive experimental evidence of the LLCP has not been obtained because of the rapid crystal-lization of liquid water in the "no-man's land." Here, we observed experimentally the pressure-induced polyamorphic transition in the dilute glycerol-water solution which relates to the water polyamorphism. We examined the effect of the glycerol concentration on the liquid-liquid transition, and found its LLCP around 0.12–0.15 mole fraction, 0.03–0.05 GPa, and ~150 K. A 150 K was above, or around, the recently recognized glass transition temperatures of amorphous ices, and the crystallization did not occur, indicating that the direct observation of LLCP is feasible. The low-temperature LLCP has implication to the argument of the relation between the interaction potential of water molecule and the polyamorphic phase diagram. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4894416]

I. INTRODUCTION

In order to understand the water polyamorphism completely,^{1,2} the direct experiments on the liquid-liquid critical phenomena are indispensable. However, the direct measurements of the liquid-liquid transition (LLT) and of the dynamics around the liquid-liquid critical point (LLCP) are practically difficult because of rapid crystallization of liquid water in the "no-man's land." There are not yet decisive experiments proving the existences of LLT and LLCP.

To avoid the crystallization many experiments on the aqueous solution systems^{3,4} and the confined water systems^{5,6} have been performed. In particular, the addition of solute elements to water tends to lower the homogeneous nucleation temperature (T_H) of the aqueous solution.^{7,8} On the other hand, the cooling of liquid sample under pressure facilitates the homogeneous vitrification of the sample.^{3,4,7–10} We have vitrified pure liquid water and dilute aqueous solution by cooling under high pressure and have reported that the solvent water in the glassy sample resembles high-density amorphous ice (HDA).^{3,9} In this experiment, we vitrified the emulsified glycerol-H₂O solution in the glycerol concentration $(C_{glvcerol})$ range of 0.02–0.12 molar fraction (mf) by cooling at 0.3 GPa and measured the isothermal volume change of the glassy sample during compression and decompression in the measurement temperature $(T_{measure})$ range of 138–154 K.

II. SAMPLE AND METHOD

A. Sample

Glycerol (Wako Chemical Co., Ltd.) was mixed with high-purity water (Millipore: Direct-Q UV). The emulsion of glycerol-H₂O solution, made by stirring the 2 g of glycerolwater solution and a matrix (1 g of methylcyclohexane, 1 g of methylcyclopentane, and 100 mg of sorbitan tristerate) was used in the isothermal volume measurements. About 1.5 ml of glycerol-H₂O solution sample was sealed in an indium container. It was compressed to 0.3 GPa at room temperature by using a piston-cylinder apparatus with a temperature controller, and cooled to 77 K at a cooling rate of ~40 K/min. In the simultaneous measurement of sample temperature, the special indium container with thermocouple was used.

Raman spectroscopy was used for the phase identification. In this Raman experiment, the bulk glycerol- D_2O solution was used without the emulsion matrix. D_2O was used because the OH- and CH-stretching modes of glycerol molecule locate around the OH-stretching mode of H_2O . The exchange between the proton in glycerol and the deuteron in D_2O , if any, did not impede the phase identification.

The lowest $C_{glycerol}$ at which the sample was vitrified homogeneously was ~ 0.02 mf for the emulsified sample and was ~ 0.07 mf for the bulk sample.

B. Isothermal volume measurement

The sample made by cooling to 77 K under 0.3 GPa was further compressed to 0.6 GPa and heated to a given $T_{measure}$. Subsequently, the sample was decompressed to 1 atm, kept at 1 atm for 2 min, and compressed to 0.6 GPa. During decompression and compression, the piston displacement was recorded. This decompression-compression-heating sequence was performed repeatedly rising the $T_{measure}$ every 2 K.

C. Data handling

In principle, we can determine the sample pressure by the force/area ratio of the piston. The error of pressure, caused by

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the friction between piston and cylinder, was reduced by using both the compression curve and the decompression curve of indium, as shown in Fig. 1(a). These compression and decompression curves changed monotonously, and they differed slightly due to the friction. The pressure of compression curve and of decompression curve were shifted by $-\Delta P$ and ΔP , respectively, so that the two curves overlapped each other at each pressure and at each $T_{measure}$. (See an inset of figure 1(a).) These ΔP values were regarded as the error caused by the friction, and they were applied to correct the sample pressure in this study.

The specific volume of the emulsion matrix without solution was calculated by subtracting the piston displacement data of the indium container with a constant mass from the piston displacement data of the emulsion matrix (Fig. 1(b)). The pressure-calibrated compression curve and the pressurecalibrated decompression curve agreed well. The compression and decompression curves were monotonous below 0.6 GPa and below 160 K, and this provided a blank test.

We directly compared the compression/decompression curves for the emulsified solution of 0.07 mf with those for the bulk solution of 0.07 mf without emulsion matrix in Fig. 1(c). These curves were measured at 150 K. Although the magnitude of each curve are different because of the difference between the amount of solution sample in each measurement, the profile of curve for emulsified sample is almost similar to that for bulk sample. This indicates that the emulsion matrix does not affect the volume change of sample solutions.

The specific volume of emulsified solution sample is calculated by subtracting the piston displacement data of both the indium container with constant mass and the emulsion matrix without solution from the piston displacement data of the sample. For example, the piston displacement data (raw data) for the emulsified glycerol-H₂O solution of 0.03 mf with various $T_{measure}$ (138–154 K) are shown in Fig. 1(d). The reproducibility of piston displacement is observed. The estimated specific volume-pressure curves are shown in Fig. 1(e).

D. Raman spectroscopic measurement

The sample made by cooling to 77 K under 0.3 GPa was recovered at 1 atm at 77 K, replaced in a cryostat with a temperature controller and cooled at 32 K. Subsequently, the intensity of the Raman scattered radiation polarized parallel to the incident light was recorded using a microscopic Raman spectrometer (Jobin Yvon Inc. T64000). The exciting light source was an argon ion laser operating at 488 nm with power of \sim 500 mW. The recorded Raman spectra were corrected by polarizer characteristics and back ground.

III. RESULT AND DISCUSSION

When the sample of 0.02 mf is decompressed, its volume increases rapidly at a certain pressure (blue curves in Fig. 2). Subsequently, when this low-density sample is compressed at the same $T_{measure}$, its volume decreases stepwise at the pressure higher than the pressure of rapid volume increase in decompression (red curves). As the $T_{measure}$ rises, the pressure



FIG. 1. Piston displacement-pressure curves and specific volume-pressure curves. (a) The piston displacement changes of indium in decompression (a blue curve) and compression (a red curve) at 150 K and the pressure calibration curve (a black curve). The expanded data are shown in an inset. The difference, ΔP , was used to determine the sample pressure. (b) The specific volume changes of emulsion matrix without sample at 150 K. The pressure-calibrated compression curve is in good agreement with the pressure-calibrated decompression curve. (c) The direct comparison of the piston displacement-pressure curves between for emulsified 0.07-mf sample and bulk 0.07-mf sample without emulsion matrix. The measurements were performed at 150 K. These data are raw data including the volume change in the indium (or both the indium and the emulsion matrix). The curves for the bulk sample are shifted vertically for clarity. (d) The piston displacement changes of emulsified glycerol-H₂O solution of 0.03 mf in compression and decompression from 138 to 154 K. These are raw data. A part of the sample was crystallized during the transition from high-density state to low-density state in decompression at 154 K (a thick black curve). When the crystallized sample was compressed at 154 K, it amorphized at ~ 0.56 GPa. (e) The specific volume changes of the emulsified glycerol-H2O solution of 0.03 mf in compression and decompression in the 138-152 K range. These data were calculated from the raw data of (d) and the pressure was obtained by using ΔP of (a). Negative pressures in Figs 1(a), 1(c), and 1(d) correspond to the "down load" of the press. Note that the volume near 1 atm may be influenced by the deformation of the press, the pressure-sealing device, the indium container, and so on.

at which the stepwise volume increase occurs in decompression (P_{H-to-L}) shifts toward the higher pressure side and the



FIG. 2. Isothermal volume changes of emulsified glycerol- H_2O solutions. The decompression and compression curves are drawn by blue and red, respectively. The samples of 0.02 mf, 0.03 mf, and other concentration crystallize during decompression at 152, 154, and 156 K, respectively. The volume changes of crystallized sample are omitted. The isothermal volume changes except for one at 142 K are shifted vertically for clarity.

pressure at which the stepwise volume decrease occurs in compression (P_{L-to-H}) shifts toward the lower pressure side. Both stepwise volume changes are accompanied by heat generation (Figs. 3(a) and 3(b)).

Next, with the increase in $C_{glycerol}$ the slope of the stepwise volume change becomes smaller and the gap size at the stepwise volume change becomes small (Fig. 2). When the $C_{glycerol}$ approaches 0.12 mf, the isothermal volume change becomes monotonous without stepwise.

In order to examine the structural difference between the high- and low-density samples, we vitrified bulk glycerol-D₂O solution of 0.07 mf by cooling to 77 K at 0.3 GPa and decompressed it to 1 atm. The sample was heated up to a given temperature (140 K and 170 K), cooled to \sim 32 K, and then its Raman spectrum was recorded at \sim 32 K. The high-density sample was transformed to the low-density sample around \sim 135 K and the low-density sample was crystallized around 160 K. As indicated in both Fig. 2 and the inset of Fig. 4, the P_{H-to-L} increased with the increase in $T_{measure}$. When the high-density sample of 0.07 mf was decompressed to 1 atm below 135 K, the transition to low-density sample did not occur, and the high-density sample was recovered at 1 atm. When heated at 1 atm, it transforms to the low-density sample which must be equivalent to the low-density sample made by isothermal decompression above ~ 135 K. Raman spectra of the high-density sample, the low-density sample and the crystalline sample are compared with Raman spectra of HDA, low-density amorphous ice (LDA) and crystalline ice Ic of D_2O (Fig. 4).

The Raman profiles of the OD-stretching modes of high- and low-density sample, which correlate to topological configuration of hydrogen-bonded tetrahedral unit of water molecules,¹¹ resemble the Raman profiles of HDA and LDA, respectively. In particular, the central frequency of the largest OD-stretching band around ~ 2350 cm⁻¹ marked by an asterisk suggests that the solvent waters of the high- and low-density sample are HDA-like and LDA-like, respectively. Therefore, the stepwise volume changes of the glycerol-water solution observed below 0.10 mf are identified as a polyamorphic transition that corresponds to the LDA-HDA transition of pure water.¹²

In the decompression process of the glycerol-H₂O solution of 0.02 mf at 150 K, an endothermic event started at ~ 0.23 GPa (pressure B in Fig. 3(b)). In order to clarify the change in the slope of decompression curve round ~ 0.23 GPa, we compared in Fig. 3(c) the decompression curve of the 150-K sample with the decompression curve of the 135-K sample which was below glass transition temperature, T_a (See also Fig. 1(d)). Both decompression curves at pressures higher than ~ 0.23 GPa seem to almost overlap each other. The decompression curve for 150 K begins to deviate from that for 135 K around ~0.23 GPa (pressure B in Fig. 3(c) and its slope becomes large. This indicates that the glass-to-liquid transition of the high-density sample occurs around ~0.23 GPa at 150 K. The similar glass-to-liquid transition occurring during decompression have been observed in the LiCl-water solutions.⁴ Although the glycerol concentration would generally affect the T_g ⁸ the T_g of dilute solution observed during the decompression should relate to the T_{g} of HDA of pure water. Practically, the glass transition for the 0.02 mf sample (150 K and \sim 0.23 GPa) is in good agreement with the recent findings by Handle et al.¹³ and Seidl et al.¹⁴ for bulk pure water and the recent finding by Mishima¹⁵ for emulsified pure water. We think that, in the dilute solutions, the glycerol dissolves homogeneously in HDA; that is, the solutions become pure water continuously as the $C_{glycerol}$ decreases.

On the other hand, this experimental study cannot clarify whether the state of low-density sample at 150 K is liquid or not. We think that the T_g of the low-density glassy aqueous



FIG. 3. The simultaneous measurements of the piston-displacement change and the sample temperature change for the 0.02 mf sample at 150 K and the change in the slope of decompression curve around the glass transition. (a) and (b) The piston displacement change (green dots) and the sample temperature change (black dots) during the compression and the decompression. These data were obtained by using the container for the simultaneous measurement. The transformation between low- and high-density states accompanies large heat generation (pressure A and C). In the decompression process, the onset of volume increase coincides with a small elevation of sample temperature (pressure C). After that, the sudden and large heat generation at pressure D is observed later because of a competition between the heat-absorbing of rapid quasi-adiabatic expansion and the heat-generation of polyamorphic transition. The endothermic event occurred around 0.23 GPa (pressure B) in the decompression process. (c) The decompression curves of the 0.02-mf sample at 135 K (pink) and 150 K (green). The sample temperature was not measured simultaneously.

solution with low concentrations should relate closely to the T_g of LDA. Recent reports have indicated that T_g of well-relaxed LDA at 1 atm lies at ~136 K¹⁶ and the T_g lowers with the increase in pressure.¹⁷ According to T_g ~136 K of LDA,¹⁶ the low-density sample of 0.02 mf at 150 K is already viscous liquid. This suggests that a reversible, not one-way, LLT occurs.



FIG. 4. Raman spectra of high-density, low-density, and crystalline glycerol-D₂O solution of 0.07 mf. The low-density sample and crystalline sample were made by heating at $T_a = 140$ and 170 K, respectively. For reference, the Raman spectra of HDA, LDA, crystalline ice Ic of D₂O, and pure glycerol are shown. All Raman spectra were recorded at ~32 K. The bands appearing around 2800–3000 and 3100–3600 cm⁻¹ are assigned as the CH-stretching modes and the OH-stretching modes of glycerol molecule, respectively (Ref. 34). An inset is a schematic phase diagram relating to the transformation from high-density state to low-density state of the 0.07-mf sample. The starting high-density sample is made by heating at 1 atm is equivalent to the lowdensity sample made by isothermal decompression at high temperature.

The onset and offset P_{L-to-H} and the onset and offset P_{H-to-L} for the samples of 0.02–0.08 mf are plotted as a function of $T_{measure}$ in Fig. 5. Although the hysteresis between P_{L-to-H} and P_{H-to-L} depends on the observation time scale because of the transition occurring under a non-equilibrium condition, the thermodynamic transition between two states, that is the LLT, should exist somewhere between the onset P_{L-to-H} and the onset P_{H-to-L} and it is roughly expected that the LLCP locates near the intersection of the onset- P_{L-to-H} curve and the onset- P_{H-to-L} curve. It is found that, with the increase in $C_{glycerol}$, the region between the onset- P_{L-to-H} curve and the location of LLCP shifts toward the lower temperature side as the $C_{glycerol}$ increases.

Here, the P_{H-to-L} and the P_{L-to-H} at 150 K were plotted as the function of $C_{glycerol}$ in Fig. 6. The onset P_{H-to-L} and the onset P_{L-to-H} at 150 K shift to the lower pressure side as the $C_{glycerol}$ increases and the gap size between the onset P_{H-to-L}



FIG. 5. $T_{measure}$ dependence of polyamorphic transition of glycerol-H₂O solution with various $C_{glycerol}$. The onset P_{H-to-L} , offset P_{H-to-L} , onset P_{L-to-H} , and offset P_{L-to-H} for the glycerol-H₂O solutions of 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, and 0.08 mf are presented by filled blue squares, opened blue squares, filled red circles, and opened red circles, respectively. Grey hatched areas stand for the kinetic hysteresis regions relating to the transition between high- and low-density states.

and the onset P_{L-to-H} becomes small. On the other hand, as the $C_{glycerol}$ increased the difference between onset P_{H-to-L} and offset P_{H-to-L} and the difference between onset P_{L-to-H} and offset P_{L-to-H} became large.

Biddle *et al.*¹⁸ have suggested that the LLT of common aqueous solution has a co-existence area of high-density and low-density states. Practically, dilute lithium chloride, LiCl, aqueous solutions have separated into the LDA-like state that is water-rich and the HDA-like state that is solute-rich.³ We think that there is a similar coexistent region of both high- and



FIG. 6. $C_{ghycerol}$ dependence of polyamorphic transition of glycerol-H₂O solution at 150 K. The onset P_{H-to-L} , offset P_{H-to-L} , onset P_{L-to-H} , and offset P_{L-to-H} are shown by blue fill squares, blue open squares, red fill circles, and red open circles, respectively. The grey area is a supposed co-existence area of high-density and low-density states. According to Ref. 19, the blue and red dashed curves are the thermodynamic stability limit of HDA-like and LDA-like states, respectively. The LLCP of glycerol-H₂O solution at 150 K will exist somewhere in a black ellipse of 0.11–0.13 mf and 0.03–0.05 GPa. A grey broken line is a presumable Widom line and the ripples represent the fluctuation around the Widom line.

low-density states in the glycerol-water system. The increase in the difference between onset P_{H-to-L} and offset P_{H-to-L} with the increase in the $C_{glycerol}$ as shown in Fig. 6 suggests the existence of co-existence region such as shown by a grey area. The co-existence region must be limited, because, outside the region, the glycerol molecule dissolved in both HDAand LDA-like solvent waters. This homogeneous dispersion of glycerol molecule in solvent water is suggested by a good reappearance of the low- and high-density states in the repetitive compression-decompression process as shown in Fig. 1(d). If glycerol molecule did not dissolve in LDA-like (or HDA-like) water, and if the phase separation remained in the solution, the volume-pressure curves will differ during the repetitive process. The reversible LLT appeared to occur in the 0.10-mf solution, indicating that a lot of glycerol molecules dissolve in both HDA- and LDA-like solvent water. It seems that the glycerol molecule in the solutions below 0.10 mf does not hamper the polyamorphic transition.

We define the location where the LLT disappears as the LLCP of glycerol-H₂O solution. The isothermal volume measurement of the sample of 0.10 mf at 150 K in Fig. 2 shows that a subtle hysteresis of transition between high- and low-density states exists. However, the isothermal volume change for the 0.12-mf sample at 150 K has no hysteresis and the transition between high- and low-density states disappeared. Therefore, we estimate that the LLCP of the glycerol-H₂O solution at 150 K exists in the area of 0.12–0.14 mf and 0.03–0.05 GPa. Since the T_g of LDA is expected to be lower than \sim 136 K,¹⁶ the LLCP of the glycerol-H₂O solution at 150 K lies above, or around, the T_g , indicating that the direct experiment on LLCP is feasible.

We extrapolated the LLCP line to the region of 0.12–0.15 mf at 1 atm (Fig. 6), that was defined as a Widom line.^{19,20} The anomalous behaviors of glycerol-water solution at 1 atm,



FIG. 7. Schematic pressure-temperature-concentration (*P*-*T*-*c*) phase diagram of glycerol-H₂O solution from a viewpoint of water polyamorphism. Hypothetical LLCL is represented by a red broken line. The surface surrounded by the hypothetical LLCL and the grey broken lines relating to the Widom lines is expressed as a Widom surface. The ripples represent the fluctuation around the Widom lines. The grey area in the *P*-*c* plane at 150 K is the coexistence area relating to the LLT. T_H , T_x , and T_g are the cooling-induced homogeneous nucleation temperature relating to the crystallization to ice Ih, the heating-induced crystallization temperature, respectively (Refs. 8 and 21). T'_H is T_H of the emulsified glycerol-H₂O solution measured in this study.

for example, the sudden change in the $C_{glycerol}$ dependence of T_g and the rapid increase in the slope of T_{H} ,²¹ seem to occur in the fluctuation regions near the estimated Widom line.

Since the LLCP of H₂O which has been calculated from experimental data of supercooled liquid water locates in the region of 0.02-0.05 GPa and 221-225 K,^{22,23} the liquidliquid critical pressure of glycerol-H₂O solution at 150 K is the almost same as that of pure H₂O. Applying the parallel relation between the T_H line relating to ice Ih and the LLT line as proposed in pure water²⁴ and aqueous solution system⁴ to the glycerol- H_2O system, we simply draw a liquidliquid critical line (LLCL) between the LLCP of H₂O and the LLCP of glycerol-H₂O solution at 150 K being parallel to the temperature-concentration (T-c) plane at 1 atm, as shown by LLCL in Fig. 7. The actual feature of LLCL may be more complicated and we can suppose the alternative LLCL. However, this experimental result, at least, suggests that the glycerol- H_2O solution at 1 atm above ~150 K is a single phase and the first-order polyamorphic transition does not occur at 1 atm above ~ 150 K.

Our conclusion is contradictory to the recent experimental result that the LLT has occurred in the glycerol-water solution of 0.178 mf at ~171 K and 1 atm.²⁵ We have rechecked the result reported in Ref. 25 by the Raman spectroscopic study and have identified the solvent state in the glassy glycerol-water solution by comparison between the Raman profiles of glycerol-water solution, LDA, HDA, and ice Ic (Ih) which have been recorded in the same temperature condition of ~32 K (see the Appendix). As the result, we have concluded that the state of glassy glycerol-water solution made by cooling at 1 atm is not categorized in the typical HDA group and that the nature of transformation occurring at \sim 171 K in Ref. 25 is crystallization which may relate to the Widom line.

Glycerol is used as an antifreeze material for cryopreservation of living cell. When a small amount of glycerol dissolves in water, the glycerol molecule would reduce the tetrahedrality of the hydrogen-bonded network of water molecules because of the hydrogen-bonding interaction between glycerol molecule and water molecule. Indeed, the Raman profile of low-density glycerol-D₂O solution in Fig. 2 is more blurred than that of pure LDA, suggesting that the tetrahedral unit of solvent water in the low-density solution is more distorted. As the $C_{glycerol}$ increases, the stepwise volume change relating to LLT changes from sharp transition to broad transition gradually and then finally the stepwise LLT disappears. Because of this observation, we propose the existence of LLCP. It is suggested by simulations and theoretical studies^{26–33} that the decrease in the tetrahedrality of hydrogen-bonded network of water correlates strongly to the polyamorphic phase diagram; as the tetrahedrality of water becomes weaker, the liquidliquid critical temperature lowers and the behavior of LLT changes. Actually, the sign of criticality was hardly observed near the LLCP (150 K, 0.03-0.05 GPa, 0.12-0.14 mf) in this study. The critical phenomena at low temperatures may be different from that at high temperature. Further experimental studies relating to the low-temperature liquid-liquid critical phenomena are necessary. In this context, the glycerol-water solution seems to be one of the appropriate systems for the experimental studies of the effect of the interactions between water molecules, because direct LLT and LLCP experiments, relating to the water polyamorphism, are feasible in this aqueous solution.

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APPENDIX: IDENTIFICATION OF SOLVENT STATE OF GLYCEROL-H₂O SOLUTION OF 0.17 mf MADE BY COOLING AT 1 atm

We experimentally rechecked the identification of Raman spectra of glassy glycerol-water solution which have been reported by Murata and Tanaka.²⁵ Using the methods same as their experiment, we vitrified the glycerol-H₂O solution of 0.17 mf by cooling at 1 atm, kept it at 170 K and examined the transformation of the glassy sample using Raman spectroscopy. We have carried out the Raman measurements at 170 K and 32 K. The 170 K-recorded Raman spectra of the sample kept at 170 K for 5, 30, 60, and 90 min are shown in Fig. 8(a). The Raman spectra of LDA, HDA, and crystalline ice Ic, which have been recorded at ~32 K, are shown as the references.³⁵ These results for the 170 K-recorded Raman spectra are the same as the results shown in Figure 3(a) of Ref. 25.

The 170 K-recorded Raman spectrum of the sample kept at 170 K for 5 min is apparently similar to the 32 K-recorded



FIG. 8. High-frequency Raman spectra of glycerol- H_2O solution of 0.17 mf made by cooling at 1 atm. (a) The 170 K-recorded Raman spectra of sample which were kept for 5, 30, 60, 90 min at 170 K. Raman spectra of HDA, LDA, crystalline ice Ih (Ic), and pure glycerol were measured at \sim 32 K. HDA was relaxed by annealing at 1 atm (Ref. 35). Black and red vertical broken lines represent the peak positions of the largest OH-stretching band of LDA and of ice Ih, respectively. (b) The 32 K-recorded Raman spectra. After the sample was kept at 170 K for 5, 30, 60, 90 min, it was cooled to \sim 32 K and the Raman spectra were measured.

Raman spectrum of relaxed HDA and the position of the largest OH-stretching band around 3150 cm^{-1} seems to agree with the position of the largest OH-stretching band in the Raman spectra of HDA. In addition, the 170 K-recorded Raman spectrum of sample kept at 170 K for more than 30 min seems to resemble the 32 K-recorded Raman spectrum of LDA. This similarity between Raman profiles of glycerol-H₂O sample and Raman profiles of two amorphous ices became one of the grounds of the LLT of glycerol-H₂O solution in Ref. 25. We think, however, it is inappropriate that the 170 K-recorded Raman spectra are compared with the Raman spectra of two amorphous ices which are recorded at different temperature of ~32 K.

In general, when the measurement temperature decreases, the OH-stretching band of water molecule shifts toward the lower frequency side and its Raman profile becomes sharper. As soon as we kept the sample at 170 K for 5 (30, 60, and 90) min, we cooled it down to 32 K rapidly and then we measured the Raman spectra of the sample at 32 K. As shown in Fig. 8(b), the 32 K-recorded Raman spectrum of the sample kept at 170 K for 5 min is sharper than the 170 K-recorded Raman spectrum and its Raman profile deviates from that of HDA. Moreover, the central frequency of the largest OH-stretching band is about 3108 cm⁻¹ and coincides with that of the corresponding band of LDA rather than HDA. According to our result in this paper, the LLT does not occur in the glycerol-water solution at 1 atm and the glassy state of glycerol-water solution of 0.17 mf lies near the Widom line. Therefore, we think that the glassy state is the fluctuating state between LDL and HDL.

On the other hand, the 32 K-recorded Raman spectrum of the sample kept at 170 K for more than 30 min is very similar to the 32 K-recorded Raman spectrum of crystalline ice Ic (Ih). The central frequency of the largest OH-stretching band (\sim 3077 cm⁻¹) coincides with that of the corresponding band of ice Ic. This similarity between Raman profiles points out that the sample kept at 170 K for more than 30 min is crystalline not LDA(LDL)-like glass.

Next, we measured the low-frequency Raman spectra of the 170 K-annealed samples at \sim 32 K. (See Fig. 9.) The modes in the range from 150 to 350 cm⁻¹ relate to the



FIG. 9. Low-frequency Raman spectra of glycerol- H_2O solution of 0.17 mf made by cooling at 1 atm. After the sample was kept at 170 K for 5, 30, 60, 90 min, it was cooled to \sim 32 K and the Raman spectra were measured. A red vertical broken line represents a peak position of the characteristic intermolecular vibration band of ice Ic. Several plasma lines are omitted from all spectra.

O-O-O stretching vibrational modes of a hydrogen-bonded tetrahedral unit.^{36,37} Therefore, the information obtained from the low-frequency Raman spectra more reflects the topological structure of hydrogen-bonded network than that obtained from high-frequency Raman spectra. The low-frequency Raman spectra of the sample kept at 170 K for 5 min is similar to that of LDA rather than HDA, though it is not completely same as that of LDA. The low-frequency Raman spectra of the sample kept at 170 K for more than 30 min is similar to that of Ice Ic.

In conclusion, the high- and low-frequency Raman spectroscopic studies suggest that the state of the glassy glycerolwater solution of 0.17 mf made by cooling at 1 atm is not HDA-like and that the state of the sample kept at 170 K for more than 30 min is crystalline. We think that the transformation of glycerol- H_2O solution occurring at 170 K at 1 atm relates to a crystallization of glass, not a LLT.

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