Liquid-Liquid Critical Point in Heavy Water

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According to the liquid-liquid critical-point hypothesis about water, two liquid waters exist at low temperatures and are supposed to be merged at a critical point. The low-temperature metastable melting curves of D_2O ices have been measured. It is found that the melting curve of D_2O ice III is smoothly curved around 25 MPa and 238 K, whereas the melting curve of D_2O ice IV undergoes an abrupt change of slope at 100 MPa and 220 K. This is consistent with the existence of a liquid-liquid critical point in the region between the melting curve of D_2O ice III and the melting curve of D_2O ice IV.

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The relationship between liquid, supercooled and glassy water is an active topic of research [1,2]. Several papers deal with the liquid-liquid critical-point hypothesis about water [3–7] that assumes the existence of two different liquid phases at low temperatures. Although these papers predict the location of a critical point at which the two liquids are merged, decisive experimental evidence for the critical point is lacking [8,9]. This is because, even if the point exists, it is thought to lie in the "no-man's-land" [2] where liquid water cannot be studied by direct experimental means due to the eventual freezing of the low-temperature liquid [10,11].

We can probe liquid water in this freezing region with the help of melting curves of ices [9,12]. If the critical point exists at a certain pressure and temperature, and if the melting curve of an ice phase is located on the high-temperature side of the point, the melting curve should be smooth and continuous, because there is only one liquid phase at high temperatures. At low temperatures below the critical point, the liquid would separate into two liquid phases along the liquid-liquid transition line which starts at the critical point. If the melting curve of another ice phase lies at temperatures below this critical point, we expect a discontinuous behavior of the melting curve at the liquid-liquid-crystal triple point on the liquid-liquid transition line.

We have already observed the discontinuous behavior of the melting curve of H_2O ice IV at 105 MPa and 215 K and related it to the possible liquid-liquid-crystal triple point [9]. We have since observed another discontinuous behavior of the melting curve of H_2O ice V at 75 MPa and 223 K. We have also found difficulty in studying the continuity for the melting curve of H_2O ice III around 228 K near 1 bar because the curve lies very close to the temperature axis. Here we measure the melting curves of D_2O ices, examine the continuity of these curves, and study the possibility of the existence of the critical point from this "continuity/discontinuity" judgment.

The melting curves were acquired by changing the pressure of an emulsified D_2O ice sample at different temperatures and by detecting a change in the sample temperature at its pressure-induced melting point [9,12]. The D_2O ice emulsion is used to avoid the complication of crystal-crystal transformations interrupting the melting precess. About 1.3 g of water emulsion made by stirring together methylcyclohexane (1.5 cm^3), methylcyclopentane (1.5 cm^3), heavy water (99.75% D_2O, 2 cm^3), and sorbitan tristerate (100 mg) is loaded into an indium cup and compressed in a steel cylinder (bore diameter 15 mm). The sample temperature is measured to $\pm\sim0.5$ K by a thermocouple brought into the sample through a small hole in a piston. Various ice phases are made by changing the pressure and temperature of the sample. The nominal pressure of the sample and the cylinder temperature are automatically controlled and changed along a pressure-temperature path programed beforehand. These data, as well as the sample temperature, are acquired automatically. Real pressure in the sample is obtained to $\pm\sim5$ MPa by calibrating the nominal pressure at atmospheric pressure. Error in the measured pressure due to the "friction" of the apparatus near 1 bar is reduced using a special hydraulic press with two oil-pressure systems.

Compression- and decompression-induced melting at high temperatures is detected by the decrease in sample temperature caused by the latent heat at the melting. One also obtains a line of homogeneous-nucleation temperatures (the T_H line) by detecting the temperature rise caused by freezing of supercooled heavy water. Below T_H, the sample temperature usually increases gradually on approaching the melting pressure and shows a subsequent sudden rapid increase when the sample pressure crosses the extrapolated melting curve. This sudden temperature increase may be regarded as the heat evolution due to the endothermic melting and the following immediate exothermic freezing [12]. Thus, the onset of this rapid increase in the sample temperature may be defined as the melting point below T_H. These gradual and subsequent rapid changes below T_H are also detected by the change in sample volume [12]. At much lower temperatures, the gradual temperature rise becomes predominant and

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interrupts the detection of the rapid temperature change at the melting.

The measured D_2O melting curves and the D_2O-T_H line are shown in Fig. 1. These curves agree with the reported D_2O melting curves [13,14] (and the T_H line [11]) in the region of overlap, showing accuracy of this experiment. In Fig. 1, we can see a discontinuity in the slope of the ice IV melting curve at 105 MPa and 219 K and an apparently discontinuous behavior of the ice V melting curve at 75 MPa and 226 K. The melting curve of ice I*h* and that of ice XIV cross smoothly over the T_H line. The melting curve of ice III is smooth though it strongly curves when it crosses over the T_H line around 25 MPa and 238 K. These D_2O melting curves and the D_2O-T_H line resemble those of H_2O, confirming the reported results for H_2O melting curves [9]. The D_2O curves are shifted by about 3 K to the high-temperature side compared to the H_2O curves. We recall that this shift to higher temperature for D_2O is also observed for other properties such as melting point and temperature of maximum density.

The melting curve generally reflects the properties of the crystal and liquid states. Smoothness of the melting curve indicates that thermodynamic properties of both the crystal and the liquid phases change smoothly along the curve. Therefore, thermodynamic properties of the liquid change smoothly along the smooth melting curves of ice I*h* and ice XIV down to 170–180 K. The rather strong bend of the ice III melting curve around 0–0.2 GPa is, no doubt, related to the peculiar behavior of supercooled water in this pressure-temperature region [15–17].

The abrupt changes in slope of the ice V and ice IV curves are considered to be caused by either a discontinuous change in the liquid state or a discontinuous change in the ices. Very likely these changes in slope are caused by a change in the liquid state, because these changes occur near the T_H line which is related to the liquid, not to these high-pressure ices. It would be irrational to consider that thermodynamic properties of different ices change accidentally near the T_H line. It should also be noted that the homogenous nucleation phenomenon in a liquid—or the T_H line—does not actually affect melting curves of crystals, as demonstrated by the smoothness of the melting curve of ice I*h* and that of ice XIV in crossing over the T_H line. Therefore, the observed changes in slopes of the melting curves of ice IV and ice V are considered to be caused by some discontinuous behavior of the liquid water around 0.1 GPa and 220 K.

The melting curves in the 0–0.2 GPa and 200–250 K region are shown in the left panel of Fig. 2. Although strongly curved, the ice III melting curve is smooth within the experimental uncertainty. Contrarily, ice IV appears to have a clear discontinuity in its slope. The apparently discontinuous behavior of the melting curve of ice IV and the smoothness of the melting curve of ice III are consistent with the existence of the liquid-liquid critical point in the region between the ice-III and ice-IV melting curves, as shown in the right panel of Fig. 2. Ice V also appears to have a discontinuity in the slope of its melting curve,

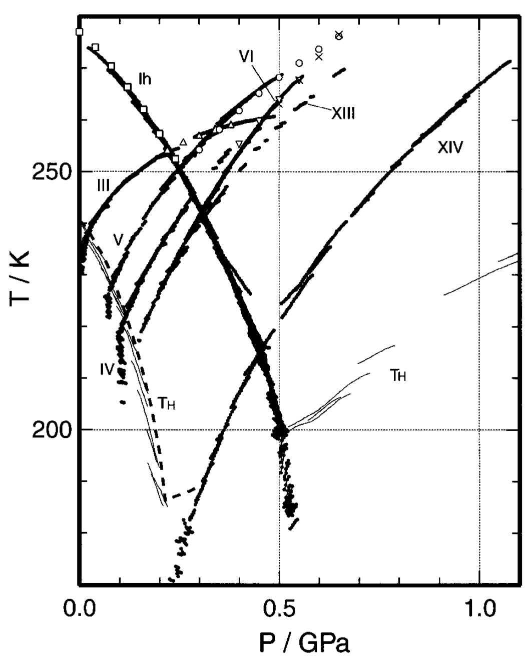

FIG. 1. The melting curves of D_2O ice I*h*, III, V, VI, XIII, and XIV. The sample temperatures at melting are plotted versus pressure. The sample temperature decreases at compression- or decompression-induced melting above T_H, while it apparently increases at melting below T_H. The markers are previously measured melting points [13]: (□) I*h*, (△) III, (○) V, (▽) IV, (×) VI. The fine solid lines and the dotted line are, respectively, the T_H lines of D_2O determined in the present study and reported in Ref. [11]. The high pressure part of the T_H line beyond the minimal pressure of 0.2 GPa, which is determined in this study, resembles that of H_2O [9].

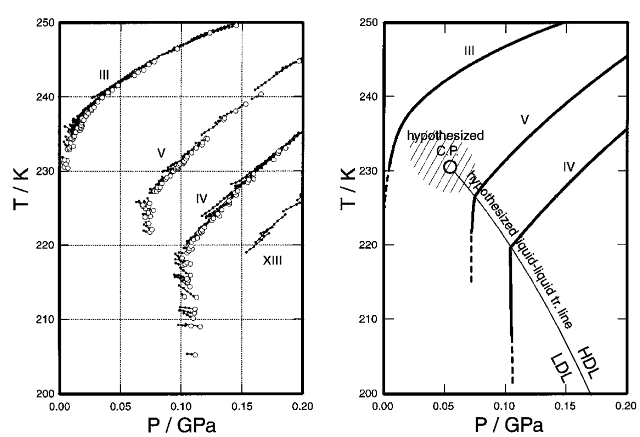

FIG. 2. The melting curves of D_2O ices (III, V, IV, XIII) in the region of 0–0.2 GPa and 200–250 K. Left: experimental results. The empty circles are the onset of the change in the sample temperature. Right: schematic representation of the hypothesized first-order liquid-liquid transition line dividing the low- and high-density liquids (LDL and HDL) and the liquid-liquid critical point (C.P.). The C.P. is thought to exist in the hatched area.

but it is difficult to conclude from the present data that the melting curve of ice V truly exhibits this discontinuity. If it is discontinuous, the critical point would be located between the melting curve of ice III and the melting curve of ice V—somewhere in the hatched area in Fig. 2 (about 50 ± ~20 MPa and 230 ± ~5 K). It is noteworthy in this connection that low-temperature extension of the empirical equation of state for H_2O fluid [18] shows a critical-point-like behavior at 60 MPa and 221 K; the location is near the present D_2O critical point. The melting curves of D_2O ice VI and D_2O ice XIII are expected to exhibit discontinuities at the liquid-liquid transition line, but their melting curves near the line have not been measured in this study because of experimental difficulties.

In the high-pressure high-temperature region above the hypothesized liquid-liquid transition line in Fig. 2 (in the upper-right part of the figure), the curvature of the convex melting line of ice III is larger than that of ice IV. The curvature is considered to imply the degree of the change in the liquid state along the melting curve, because the changes in solid ices are usually relatively small. The strong curvature along the ice III line is consistent with the large change in the liquid state above the critical point, whereas the rather straight line of ice IV is consistent with small changes in the high-pressure liquid phase.

According to the stability-limit conjecture [19,20], which is another water model, liquid water cannot exist below the so-called spinodal temperature T_S. If this conjecture is correct, heavy water would become unstable and would show some strange behavior as it approaches T_S of D_2O (about 230–235 K at 1 bar [16,20]) because there is no liquid state below T_S. Then, the instability would affect the melting curves or there would be a discontinuity in slope due to the liquid-liquid first-order transition above T_S [4]. However, the melting curve of ice III actually continues smoothly to 230 K near 1 bar, indicating existence of the liquid state near T_S and probably below. Thus, the existence of the singular point T_S is questionable at 1 bar.

The steep positive slope of the ice III melting curve near 230 K (Fig. 2) indicates, from the Clapeyron relation, a large difference in volume between ice III and the liquid and/or small difference in entropy. Therefore, the D_2O water at 230 K is suggested to be low density and/or to have small entropy. These properties are also suggested from the almost vertical slope of the curves of ice IV and ice V below their discontinuities in slope, although these vertical lines have not been definitively identified as the melting lines of the low-density liquid. The cause of the apparently slightly negative slope of the ice IV line is presently unknown, but the error bars may account for it.

In conclusion, the presently available melting curves are consistent with the existence of a liquid-liquid critical point at a positive pressure, likely around 50 ± ~20 MPa and 230 ± ~5 K. Smoothness of the melting curve of D_2O ice III and discontinuous behavior of the melting curve of ice IV (and probably ice V) were observed. The present experimental results may have implications not only for studies on water and aqueous solutions, but also for our understanding of other liquids [21].

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