In-situ Raman study of the pressure-induced bulk melting of hexagonal ice

Yukihiro Yoshimura*1, Ho-Kwang Mao2 and Russell J Hemley2
1 Department of Applied Chemistry, National Defense Academy, Yokosuka, Kanagawa 239-8686, Japan
2 Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Rd. N.W., Washington, DC 20015, U. S. A.
* E-mail: muki@nda.ac.jp

Abstract
We have investigated a series of changes in in-situ Raman spectra as a function of pressure at 264 K to study the process of bulk melting in Ih (hexagonal ice) to the liquid water. We succeeded in measuring spectra where ice Ih coexists with liquid water at an equilibrium pressure of 0.1 GPa. The lowest frequency peak which is derived from the strong hydrogen-bonds of ice Ih lattice remains until the transition and the fraction of liquid water at this equilibrium increases upon compression. The results are interpreted in the context of pre-melting effects in the ice particles.

1. Introduction

The high-pressure polymorphism of H2O ice is a subject of continuing interest. Although at least 15 different stable and metastable forms [e.g., ice Ih, Ic to XII, low-density amorphous ice (LDA), and high-density amorphous ice (HDA)] have been identified so far [1-7], very recently two new hydrogen ordered phases of ice, referred as ice XIII and XIV, have been found by doping hydrogen disordered phases of ices V and XII with HCl [8]. Our understanding of the phase diagram of H2O is still incomplete, especially at low temperatures and modest pressures.

One of the most peculiar features of H2O is that the melting curve for ice Ih against pressure has a negative slope. This is due to the fact that ice melts upon compression; by Le Chatelier’s principle, this causes icebergs to float on water.

In this study, we have examined the pressure-induced phase transformations of ice Ih-liquid water at ~264 K as a function of pressure by monitoring the in-situ Raman spectral changes. We will show vibrational dynamics of the internal modes combined with the low frequency spectra studied by the low temperature Raman spectroscopy, which are powerful indicators of the phase transitions. As far as we know, apparently there have been no studies of the spectra under high pressure. One could in fact imagine that melting takes place either as a sudden collapse of the lattice or through the creation and successive catastrophic multiplication of defects. We succeeded in catching the spectra where ice Ih coexists with the liquid water at an equilibrium pressure of 0.1 GPa. The results are interpreted in view of the premelting effect in the ice particles.

2. Experimental details

Raman spectral changes were measured in-situ by microspectroscopy together with a Mao-Bell diamond anvil cell (DAC) and a cryostat system at high pressures and low temperatures, as described in detail earlier studies [9].

H2O ice was made from doubly distilled deionized water [Figure 1 path (1)]. The sample water and a few
ruby chips were held in a DAC using a stainless steel gasket. To determine the pressure, we used the pressure dependence on the spectral shift of the $R_1$ fluorescence line of the ruby chip [10, 11]. A DAC equipped with two heaters and thermocouples was cooled to ≈265 K in a continuous-flow of liquid nitrogen. The cryostat was equipped with windows, which allows for in-situ Raman (and also ruby fluorescence) measurements without changing the $P$-$T$ conditions on the sample. Pressure can be controlled from the outside by a mechanical change in the load on the DAC lever arms. The temperature was measured to within ±1 K.

Raman spectra were collected by a single-grating ISA HR-460 spectrometer equipped with holographic notch filters and a charge-coupled device (CCD) detector. The 514.5 nm line of argon ion laser excitation (~300 mW) was selected to use.

3. Results and Discussion

The experimental paths performed in this study are shown schematically on the pressure-temperature equilibrium phase diagram of H$_2$O in Fig. 1. First, ice Ih was made by cooling the sample water held in a DAC in a cryostat up to 264 K [path (1)]. Then, gradually we kept compressing ice Ih at 264 K [path (2)]. We measured the in-situ Raman spectral changes of OH stretching vibrational and low-frequency modes of path (2) as depicted in Figs. 2 and 4.

Figure 1. The experimental path observed in the present study on the equilibrium phase diagram of H$_2$O. The indication corresponds to the results of Raman spectral changes as shown in Figs. 2 and 3, respectively.

Figure 2 shows in-situ Raman OH-stretching spectral changes as a function of pressure at 264 K. We note first that the relative intensity of the band centered at ~3300 cm$^{-1}$ increases gradually with increasing pressure. Close to the equilibrium melting pressure, the structure of the spectrum changes very slowly. This change must illustrate that the equilibrium crystal structure has been transforming into a liquid structure. We note that the lowest frequency peak that is characteristic of ice Ih phase remains until the transition occurs. We succeeded in obtaining the mixture (coexistent) state spectra between ice Ih and the liquid water, meaning spatially inhomogeneous. It is obvious that at around 0.1 GPa the sample completely transformed to liquid
water. The spectrum for water is relatively broad, because of the increase in the distribution of energy state. The features of the spectrum in the OH stretching vibrations region have been discussed by several workers [12-16] and assigned to the various intermolecular modes. Since the origin of its several low frequency features remains uncertain, we would, therefore, proceed with our discussion without reviewing the origin of this feature.

Photomicrographs showing the changes of a representative sample are shown in Fig. 3. Liquid water began to grow as a small region showing a meniscus within ice Ih; upon further compression complete melting to liquid water occurred. Then the sample finally crystallized to ice V (image 4).

![Image of photomicrographs showing the transformation from ice Ih to liquid water, then finally to ice V.](image)

**Figure 3.** Photomicrographs showing the transformation from ice Ih to liquid water, then finally to ice V. Image 2 shows the mixed phase parts of the sample during the course of the transition. Liquid water is the left portion of images 2 and 3. Upon further compression complete crystallization to ice V occurred, as shown in image 4.

We have also measured the Raman spectra of translational vibrations region. Figure 4 shows the Raman spectral changes of the low-frequency mode. With increasing pressure, the band shoulder at \( \sim 280 \text{ cm}^{-1} \) gradually disappears and begins to grow at the expense of the broad signal (band) of water. We can recognize that the sharp peak at 210 cm\(^{-1}\) of ice Ih was found to remain until the transition occurs: the situation was in harmony with the results of OH-stretching mode. Thus, an important point here is that the ice Ih changed to liquid water showing the mixture state of ice Ih and liquid water, not forming other intermediate structures, as we decreased the pressure little by little. This result confirms that the phase transition between ice Ih and liquid water is first-order one. This transition is sharp, being completely achieved by a pressure change of \( \sim 0.02 \) GPa. We tried to monitor the pressures of the sample during the measurements by the spectral shift of the \( R_1 \) ruby fluorescence line. However, at relatively lower pressure regions of around 0.1-0.2 GPa, it was difficult to obtain the precise transition pressure value due to the insensitivity of the ruby fluorescence. At these conditions, the sample pressure was determined from the change in the load on the DAC lever arms.

It is interesting to quote a pre-melting [17, 18] to interpret the mechanism of our present results. The pre-melting is provided originally to explain the coexistence of the liquid and solid phases at
temperatures substantially below the usual thermodynamic melting point. The effects of crystal size, grain junction-melting, and grain boundary melting have been subjects of considerable interest from a physical point of view. That is, ice melts to fill grain junctions, part of the grain-grain boundary vanishes, and grain-liquid interface forms at places where the grains meet and pockets of liquid form. The ice is no longer in its lowest free energy state and it melts at the grain junctions. A substantial amount of water exists in pure ice at thermodynamic equilibrium below its melting point. Such amounts of liquid in a fine grained solid at thermodynamic equilibrium will affect their compressibility, expansion coefficient, and creep and fracture behaviours.

We suggest that melting might begin from a number of independent grain boundary or junction sites distributed throughout the sample. Over pressure, the melting regions became larger, covering more of the sample, although residual ice lattice still tends to be present in the sample. Of course, as pressure was increased, more independent melting sites increase and decrease the sample remained ice Ih. The present measurements itself, unfortunately, do not provide structural details. But we suppose that the subsequent formation of coordination defects triggers the transition to the liquid state.

In conclusion, the present paper has illustrated important aspects of the complex behavior of ice viewed from the liquid and the solid sides. Our in-situ measurements provide evidence that ice Ih changed to liquid water with showing the mixture state of ice Ih and liquid water, not forming other intermediate structures upon compression. We suppose that the bulk melting is mediated by the formation of topological defects. The study of the low-temperature transitional phase diagram of ice is of practical interest for the planetary geology and astrophysical implications because many high-pressure ice polymorphs, including the amorphous modification, can be ubiquitously distributed. The in-situ measurements give us the opportunity to extract information on the kinetics of the transformation and on the properties of the intermediate states.

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