High-Pressure Phase and Elasticity of Ammonia Hydrate

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Phase stability and elasticity of ammonia hydrate have been studied using Raman spectroscopy and Brillouin scattering in diamond anvil cells up to 53 GPa and 300 K. Here we have established the high-pressure phase diagram of ammonia hydrate in three different compositions, including ammonia monohydrate (AMH, NH₃∙H₂O), dihydrate (ADH, NH₃∙2H₂O), and trihydrate (ATH, NH₃∙3H₂O). In contrast to previous experimental results, our Raman and Brillouin measurements at 300 K have shown that all three ammonia hydrates start to dehydrate at 2.1-2.2 GPa. Dehydration of the ammonia hydrate leads to the formation of single-crystal ice-VII and an increase in the concentration of NH₃ in the residual liquid. The residual liquid finally turns into solid ammonia hemihydrate phase II (AHH-II) at 4-4.6 GPa, leading to a 28% jump in the compressional-wave velocity ($V_p$). Considering a 10-15 vol.% NH₃ in the mantle of ice giants, AHH should thus be the dominant form of NH₃ coexisting with H₂O-ice in the ice giants. Further Brillouin measurements provide crucial constraints on the $V_p$ of AHH and the single-crystal elasticity of ice-VII at high pressures and 300 K. $V_p$ of AHH increases smoothly with pressure. No anomalous change in $V_p$ of AHH was identified up to 39 GPa, although a solid to solid phase transition was noted to occur at ~18 GPa by Raman measurements. In addition, as the dehydration products of ammonia hydrate, single-crystal elasticity of ice-VII has been determined up to 53 GPa at 300 K. The deviation of $C_{12}$ from $C_{44}$ observed at 11.4 and 14.6 GPa could be caused by the hydrogen bond symmetrisations or the ordering of dipole of single-crystal ice-VII. An abnormal softening in the elastic moduli $C_{11}$, $C_{12}$, and the adiabatic moduli $K_S$ together with stiffening in $C_{44}$ was observed between 42 and 53 GPa which should be caused by the transition from ice-VII to its pre-transitional state.
Of particular interest is the dramatic increase in the anisotropy of ice-VII with increasing pressure. Combining the sound velocity of AHH and ice-VII, we have modeled the $V_p$ of ice giants with a volume ratio of 20% AHH and 80% ice-VII in the mantle. The obtained high-pressure phase diagram and elastic properties of ammonia hydrate could contribute to understand the structure of the mantle in the ice giants and satellites.

**Keywords:** ammonia hydrate, AHH, single-crystal ice-VII, elasticity, phase transition, ice giants

1. **Introduction**

Hundreds of ice giants with a mean density of $\sim 1$ g/cm$^3$ and up to ten times of Earth’s mass have been discovered by recent astronomy observations (e.g. Helled et al., 2011; Rauer et al., 2014; Sotin et al., 2007; Valencia et al., 2007). The mantle of these ice giants, including Neptune and Uranus as well as their large satellites, are expected to be composed by the water-ammonia-methane mixture (e.g. Brown and Calvin, 2000; Fortes, 2012; Nettelmann et al., 2016; Sohl et al., 2003). High-pressure studies on the physical properties of the related water mixtures, particular the phase diagram, density, and elasticity, etc., are thus essential in understanding the structure, composition, and evolution of these ice giants and satellites (Choukroun and Grasset, 2010; Dong et al., 2009; Grasset and Pargamin, 2005; Kurnosov et al., 2006).

As one of the potential mantle components in the ice giants, phase stability of ammonia hydrate has been of particular research interest for many years (e.g. Cynn et al., 1989; Fortes et al., 2007; Grasset and Pargamin, 2005; Johnson and Nicol, 1987;
The high-pressure phase diagram of ammonia hydrate is complicated and strongly depends on the path-compression and the ammonia to water ratio (Fortes et al., 2007; Fortes et al., 2009; Loveday and Nelmes, 1999; Loveday and Nelmes, 2004; Loveday et al., 2009; Ujike and Tominaga, 2002; Wilson et al., 2012). Below 140 K, both ammonia monohydrate (NH$_3$∙H$_2$O, AMH) and dihydrate (NH$_3$∙2H$_2$O, ADH) crystallize into a single solid phase at high pressures (Fortes et al., 2007; Loveday and Nelmes, 2004; Wilson et al., 2012; Wilson et al., 2015; Fortes et al., 2009; Loveday et al., 2009). Between 140 and 300 K, at least 5 stable phases have been identified for both AMH and ADH at high pressures, respectively (Fortes et al., 2007 Loveday et al., 2009; Fortes et al., 2009; Loveday and Nelmes, 2004; Loveday et al., 2009; Wilson et al., 2015). Since the mantle of ice giants is at high pressures and temperatures, it is more important to explore the high-pressure stability of ammonia hydrate at higher temperatures. An early study which used neutron diffraction showed that liquid AMH would directly transform into the solid AMH-Vb phase at 2.1 GPa and 300 K (Loveday and Nelmes, 2004). In contrast, recent X-ray and neutron diffraction measurements found that elevating pressure leads to the dehydration of liquid AMH to a mixture of solid ammonia hemihydrate phase II (2NH$_3$∙H$_2$O, AHH-II) and ice-VII at 3.5 GPa and 300 K (Wilson et al., 2012). It also showed that the solid AMH-Vb phase reported by Loveday and Nelmes,(2004) is AHH-II (Wilson et al., 2012). At 19-26 GPa and 300 K, AHH-II was reported to transform into the disordered molecular alloy (DMA) (Ma et al., 2012a; Wilson et al., 2015). AHH in a sequence of ionic phases was predicted to be stable up to 500 GPa and be a separate phase coexisting with ice in the mantle of ice giants (Robinson et al., 2017).
According to the density profile and the nearby planetary nebula of Uranus and Neptune, the ammonia content is predicted to be 10-15 vol.%, indicating a composition of half ADH and half ice in some ice giants (Cavazzoni et al., 1999; Guillot, 2005). However, the phase stability of ADH at high pressures is still under debate (Fortes et al., 2007; Ma et al., 2012a; Wilson et al., 2012). At 300 K, ADH was reported to decompose into ice-VII and the residual liquid at 2.4 GPa by neutron diffraction (Fortes et al., 2007). The residual liquid from the decomposition of ADH further transforms into the AMH phase V (AMH-V) and ice-VII at 3.4 GPa and 300 K (Fortes et al., 2007; Loveday et al., 2009). However, later sound velocity and refractive index measurements have shown that liquid ADH is stable up to 3.2 GPa at 300 K, and no dehydration of ADH was observed (Ma et al., 2012b). ADH was reported to follow a similar phase transition path as AMH and would decompose into a mixture of ice-VII and AHH-II at 3.5 GPa and 300 K (Wilson et al., 2015). In this case, AHH should be a separate phase coexisting with ice-VII in the mantle of ice giants and satellites (Wilson et al., 2012; Wilson et al., 2015). More importantly, the sound velocity of AHH is unknown, and the former studied of the sound velocity of ice-VII were mostly focused on the polycrystalline (Ashahara et al., 2010; Kuriakose et al., 2017; Ahart et al., 2011; Zha et al., 1998; Polian et al., 1984). As the synthesis of single-crystal ice-VII was defective, the single-crystal elasticity of ice-VII was only studied below 8 GPa (Shimizu et al., 1995).

Here, we have studied the high-pressure phase of ammonia hydrate by combining Raman spectroscopy and Brillouin scattering at high pressures and 300 K using diamond anvil cells (DACs). We focused on the phase change of three ammonia hydrates, including AMH, ADH, and ammonia trihydrate (ATH), up to 53 GPa and
300 K. In addition, Brillouin measurements provide crucial constraints on the elasticity of ammonia hydrates and the dehydration product ice VII at high pressures and 300 K. A simple velocity model has been constructed to decipher the structure of ice giants.

2. Experiments

To explore the high-pressure phase of ammonia hydrates, high purity (99.9%) AMH was used as the starting material. Both ADH and ATH were produced by mixing AMH with deionized water in appropriate ratios. Ammonia hydrate was loaded into the diamond anvil cells (DACs) equipped with a pair of Raman ultralow fluorescence diamonds. Rhenium was used as the gasket material, which was pre-indented to a thickness of 30-40 μm. Two ruby spheres were loaded into DACs as the pressure calibrant (Mao et al., 1986). For all three ammonia hydrates investigated here, Raman measurements were performed up to ~30 GPa and 300 K at the High-Pressure Mineral Physics Laboratory in the University of Science and Technology of China (USTC). At each pressure, Raman spectra was collected at five different sample points to observe any potential phase transition and/or dehydration. Meanwhile, high-quality sample photos were taken at each pressure to capture any visual change with increasing pressure.

We have also performed high-pressure Brillouin measurements with a scattering angle of 49.3° using AMH as the starting material up to 53 GPa at 300 K at the High-Pressure Mineral Physics Laboratory in the USTC. The Brillouin signal was excited by a 500-mW laser with a wavelength of 532 nm, while the Brillouin spectra were recorded using a six-pass Sandercock tandem Fabry-Perot interferometer. The
acoustic velocities of sample were calculated from the measured Brillouin frequency shift, $\Delta\nu_B$, following:

$$v = \frac{\Delta\nu_B \lambda_0}{2 \sin(\theta/2)}$$  \hspace{1cm} (1)

where $v$ is the acoustic velocity, $\lambda_0$ is the laser wavelength of 532 nm, and $\theta$ is the external scattering angle measured outside the diamond anvil cell.

3. Results

Our high-pressure Raman measurements have revealed that AMH remained in the liquid phase at pressures below 2.2 GPa at 300 K (Figure 1). Above 2.2 GPa, some crystals started to grow from AMH inside the DACs, dividing the sample chamber into two regions (regions A and B) (Figures 1 and 2). Based on the collected Raman spectra, increasing pressure at a rate of 0.1 GPa/10 minutes finally led to the formation of one single-crystal ice-VII which filled the sample chamber excluding AHH (Figures 1 and 3). The precipitation of ice-VII leads to an increase in the concentration of NH$_3$ in the residual liquid (region A). The residual liquid was noted to completely transform to solid AHH at 4 GPa and 300 K based on the Raman measurements (Figures 1 and 2) (Ma et al., 2012a). Similar to that shown in Ma et al., (2012a), we also observed the disappearance of the stretching mode ~3342 cm$^{-1}$ at 16-18 GPa together with the presence of a new stretching mode at ~3220 cm$^{-1}$. This change was previously argued to be related to the AHH-II to AHH-DMA phase transition (Ma et al., 2012a; Wilson et al., 2015). No further change in the Raman spectra and modes were observed up to 30 GPa at 300 K. It is interesting to note that both ADH and ATH exhibited the same phase change with pressure as AMH (Figures 1 and 4). The precipitation of ice-VII from the liquid ADH and ATH occurred at 2.1-2.2 GPa. The residual liquid transformed into the solid AHH at 4-4.6 GPa and
coexisted with one single-crystal ice-VII which filled the left sample volume up to 26 GPa at 300 K (Figures 1 and 4).

We then measured the sound velocity of liquid AMH, solid AHH and ice-VII at high pressures and 300 K using Brillouin scattering (Figures 5, S1, and S2). Here, AHH and ice VII were formed by the dehydration of AMH. We only observed the compressional-wave velocity ($V_P$) of AHH in our Brillouin measurements (Figure 5). The precipitation of ice-VII from AMH at 2.2 GPa came along with an increase in the concentration of NH$_3$ in the residual liquid in region A where the composition changed from AMH to AHH. Yet the increase in the concentration of NH$_3$ did not cause any notable variation in the sound velocity or the velocity gradient of the liquid phase (Figure 5). We further observed a velocity jump in region A from 4.6 km/s at 3.7 GPa to 5.9 km/s at 3.8 GPa which was associated with the formation of solid AHH.

To examine the potential anisotropy of the polycrystalline AHH, we rotated the DACs and measured the sound velocity of AHH at a 20° step over a range of 180° at each pressure. The variation of $V_P$ over a range of 180° at each pressure was within 10%. Here, we averaged the measured $V_P$ of AHH at each pressure (Figure 5). The upper and lower bounds of $V_P$ are also shown in Figure 5.

Ice-VII precipitated from AMH formed one single-crystal which filled the sample volume excluding AHH. Ice VII is in the cubic structure with space group $Pn\bar{3}m$. Single-crystal Ice-VII is characterized by 3 independent elastic constants, $C_{11}$, $C_{12}$, and $C_{44}$ which can be derived by fitting the measured velocity using the Christoffel’s equations (Every, 1980) (Figures S1 and S2):

$$\left|C_{ijkl} n^4 \rho^2 \phi^p\right| = 0$$

(2)
where $C_{ijkl}$ is the full elastic tensor, $n_j$ and $n_l$ are the direction cosines in the photon propagation direction which can be described by the azimuthal angle $(\theta, \chi, \psi)$ of the sample platelet, $\rho$ is the density, $v$ is the acoustic velocity derived from Brillion frequency shift, and $\delta_{ik}$ is the Kronecker delta. Density of ice-VII from previous X-ray diffraction studies was combined with our measured sound velocities to determine the single-crystal elasticity of ice-VII at high pressures (Loubeyre et al., 1999; Sugimura et al., 2008). Our high-quality Brillouin results allow us to well constrain the single-crystal elasticity of ice-VII up to 53 GPa and 300 K (Figure 6 and Table S1).

Below 42 GPa, $C_{12}$ nearly equals $C_{44}$ within the experimental uncertainties except at 11.4 and 14.6 GPa. It is worth noting that both $C_{11}$ and $C_{12}$ exhibited an anomalous softening with pressure between 42 and 53 GPa together with an abnormal reduction in $C_{44}$ at this pressure range (Figure 6). Below 42 GPa, the relationship between each $C_{ij}$ and pressure ($P$) can be described as follows:

\[ C_{11} = 27.8(15) + 5.48(15) \times P - 0.173(3) \times P^2 \]

\[ C_{12} = 14.4(9) + 3.47(3) \times P \]  \hspace{1cm} (3)

\[ C_{44} = 14.7(14) + 3.35(6) \times P \]

Here, we ignored the data points at 11.4 and 14.6 GPa to derive the pressure dependence of $C_{12}$ and $C_{44}$. Using the obtained $C_{ij}$s, we have calculated the adiabatic bulk ($K_S$) and shear moduli ($G$) of ice-VII using the Voigt-Reuss-Hill average. Similar to those shown in $C_{ij}$s, anomalous softening was also observed in $K_S$ between 42 and 53 GPa but is not obvious in $G$ (Figure 6). Below 42 GPa, the pressure-elastic moduli relationship for $K_S$ and $G$ by ignoring the data points at 11.4 and 14.6 GPa is:

\[ K_S = 18.3(13) + 4.23(14) \times P - 0.0078(30) \times P^2 \]

\[ G = 10.3(6) + 2.16(7) \times P - 0.009(1) \times P^2 \]  \hspace{1cm} (4)
4. Discussion

4.1. Stability and sound velocity of ammonia hydrate at high pressures

Combining our high-pressure Raman and Brillouin measurements together with the sample photos taken at each pressure, we have found that ammonia hydrate, including AMH, ADH, and ATH, starts to dehydrate at 2.1-2.2 GPa and 300 K. The dehydration of ammonia hydrate investigated here occurs at lower pressure than that reported in previous studies (Loveday and Nelmes, 2004; Wilson et al., 2012; Wilson et al., 2015). Here we present the first experimental evidence to show how ice-VII gradually precipitates from the ammonia hydrate together with the increase of the NH₃ concentration in the residual liquid (Figure 1) (Loveday and Nelmes, 2004; Wilson et al., 2012; Wilson et al., 2015). In contrast, previous X-ray, neutron diffraction and Raman measurements suggested a direct transformation of AMH (ADH) to ice VII and solid AHH (AMH-V) (Loveday and Nelmes, 2004; Wilson et al., 2012; Wilson et al., 2015). Our experimental results confirm the speculation of Wilson et al., (2012) that ammonia hydrate with an initial H₂O to NH₃ ratio greater than 0.5 will decompose into AHH and ice-VII at high pressures. Together with our Brillouin measurements, we thus conclude that AHH is the stable form of ammonia hydrate above 4-4.6 GPa at 300 K and will coexist with ice-VII at least up to 53 GPa (Figure 4). It should be noted that, although region A experienced a change in the concentration of NH₃ due to the dehydration of AMH, the sound velocity of region A did not exhibit any anomalous change with pressure between 0.3 and 3.6 GPa (Figure 5). In addition, liquid ammonia hydrate in region A has a slightly lower $V_p$ than the pure NH₃, indicating that addition of H₂O can lower $V_p$ of the ammonia hydrate (Figure 5) (Li et al., 2009).
Above 4-4.6 GPa, AHH should crystallize in the AHH-II structure which is monoclinic with space group $P2_1/c$ (Wilson et al., 2012; Wilson et al., 2015). Previous experimental study using X-ray diffraction and Raman spectroscopy reported a phase transition from the AHH-II to AHH-DMA phase at 19-26 GPa and 300 K (Ma et al., 2012a; Wilson et al., 2015). Similar to that shown in Ma et al., (2012a), we also observed a change in the Raman stretching modes 3430 cm$^{-1}$, 3400 cm$^{-1}$, 3340 cm$^{-1}$ and 3320 cm$^{-1}$ of AHH at ~18 GPa together with the presence of a new mode at ~3220 cm$^{-1}$ for all three ammonia hydrates (Figure 2). The observed variation in the Raman stretching modes could be related to the AHH-II to AHH-DMA phase transition (Figure 2). Our Raman results are consistent with a recent theoretical calculation which found a transition from the AHH-II phase to a energetically competitive quasi-bcc AHH-DMA phase at ~20 GPa, although an X-ray and neutron diffraction study argued that this phase transition should occur at ~26 GPa and 300 K (Robinson et al., 2017; Wilson et al., 2015). It is worth noting that previous experimental studies only observed two broad diffraction peaks for the proposed AHH-DMA phase (Ma et al., 2012a; Wilson et al., 2015). Although the AHH-DMA phase could be stable up to 65 GPa at 300 K, the structure of the AHH-DMA phase cannot be well constrained by limited number of diffraction peaks and thus needs further investigation (Ma et al., 2012a; Robinson et al., 2017; Wilson et al., 2015). In addition, we did not observe any anomalous change in the sound velocity of AHH up to 39 GPa (Figure 5). The polycrystalline AHH in our DACs was not laser annealed and might have developed weak preferred orientations at high pressures. The change in the sound velocity across the phase transition obtained from the polycrystalline AHH sample could be relatively small and cancelled out when we averaged the measured velocity in different
azimuthal angles. The shaded area in Figure 5 provides the estimated errors of our sound velocity measurements for AHH. The change in the sound velocity from AHH and DMA could be within the shaded area and needs to be examined by future studies.

4.2 Sound velocity of ice-VII

As the dehydration product of ammonia hydrate above 2.1 GPa, ice-VII will be an individual phase coexisting with AHH in the mantle of ice giants and satellites (Robinson et al., 2017; Wilson et al., 2012; Wilson et al., 2015). Comparing the Raman modes of ice-VII from the dehydration of AMH to those of ice-VII from pure H$_2$O has shown that they are indistinguishable from each other within experimental uncertainties (Figure 3). Moreover, the obtained $C_{ij}$s, $K_S$, and $G$ of our ice-VII single crystals at 2.8 and 6.7 GPa are in excellent agreement with previous single-crystal measurements for H$_2$O ice-VII (Figure 6) (Shimizu et al., 1995). This indicates that ice-VII crystallized from the dehydration of AMH has a composition almost the same as that from pure H$_2$O, or the NH$_3$ content in our single-crystal ice VII is below the detection limit of the Raman and Brillouin measurements.

Here Brillouin measurements yield crucial constraints on the elasticity and structure of ice-VII at high pressures. Except at 11.4 and 14.6 GPa, $C_{12}$ of ice-VII nearly equals $C_{44}$ up to 42 GPa within experimental uncertainties because of the interaction of atoms by the central forces following the Cauchy relation, consistent with previous single-crystal measurements (Figures 6 and S3) (Shimizu et al., 1995). At 11.4 and 14.6 GPa, $C_{12}$ clearly deviates from $C_{44}$. A previous single-crystal X-ray diffraction study reported an abnormal change in the $d$-spacing of the superlattice $\frac{111}{222}$ of ice-VII between 10 and 20 GPa, which was interpreted to be caused by the ordering of
dipole following the Ising model (Loubeyre et al., 1999). Recent high-field nuclear magnetic resonance spectroscopy measurements revealed the hydrogen bond symmetrisation of ice-VII at 17 GPa (Meier et al., 2018). We speculate that the deviation of $C_{12}$ from $C_{44}$ observed at 11.4 and 14.6 GPa could be caused by the hydrogen bond symmetrisations or ordering of dipole of single-crystal ice-VII, although Brillouin measurements cannot unravel the variations of hydrous bond with pressures (Loubeyre et al., 1999; Meier et al., 2018).

We also observed an abnormal change in all the $C_{ij}$'s between 42 and 53 GPa which should be caused by the transition from ice-VII to the pre-transitional state ice-VII (Figure 6) (Asahara et al. 2010; Machida et al. 2008; Sugimura et al., 2008). The change from ice-VII to its pre-transitional state was noted to produce an slightly drop in the unit cell volume in the X-ray diffraction experiments (Sugimura et al., 2008). Previous Brillouin measurements using polycrystalline ice-VII reported a sudden drop in the shear-wave velocity, $V_s$, at 40 GPa in a much narrower pressure range (2 GPa) (Asahara et al., 2010). The sudden drop in $V_s$ was explained to be caused by the change from the ice-VII to its pre-transitional state (Asahara et al., 2010). Here we showed that the variation of ice-VII to its pre-transitional state can barely influence $V_s$.

The shear modulus, $G$, is calculated following:

$$
G_{\text{Voigt}} = \frac{(C_{11} - C_{12} + 3C_{44})}{5}
$$

$$
G_{\text{Reuss}} = \frac{5C_{44}(C_{11} - C_{12})}{[3(C_{11} - C_{12}) + 4C_{44}]}
$$

$$
G = \frac{(G_{\text{Voigt}} + G_{\text{Reuss}})}{2}
$$

Where $G_{\text{Voigt}}$ and $G_{\text{Reuss}}$ are the Voigt and Reuss bound of the bulk (shear) modulus, respectively. As a result, the softening of ($C_{11} - C_{12}$) is compensated by the stiffening of $C_{44}$. No anomalous change in $G$ and $V_s$ is observed between 42 and 53 GPa (Figures 7, S4, and S5). Meanwhile, the anomalous change in $V_p$ is much weaker than the individual $C_{ij}$s (Figure S5). The reported sudden drop in $V_s$ from polycrystalline...
measurements which strongly relied on one data point at 40 GPa with substantial
errors is thus highly questionable (Asahara et al., 2010). Furthermore, the change of
ice-VII to its pre-transitional state should occur in a wider pressure range than
reported in the previous study (Asahara et al., 2010). Single-crystal elasticity of
ice-VII has also been determined by a previous study using the measured maximum
and minimum $V_p$ of polycrystalline ice-VII (Kuriakose et al., 2017). Such method
provided indirect constraints on the single-crystal elasticity of ice-VII at high
pressures with much larger errors, which preclude the observation of the abnormal
change in $C_{ij}$s when ice-VII changes into the pre-transitional state (Figure S3)
(Kuriakose et al., 2017).

In general, both $V_p$ and $V_S$ of ice-VII calculated from our single-crystal elasticity are
in good agreement with polycrystalline measurements below 10 GPa. At higher
pressures, our $V_p$ is slightly lower than those from polycrystalline measurements,
whereas $V_S$ is greater. Since increasing pressure could change the polycrystalline
ice-VII to large anisotropy grains, measuring the acoustic velocity of polycrystalline
ice-VII at one direction may introduce large uncertainties at higher pressures (Ahart et
al., 2011; Asahara et al., 2010; Polian and Grimsditch, 1984; Zha et al., 1998). $V_p$ and
$V_S$ derived from single-crystal elasticity are thus more reliable than those from
polycrystalline measurements. Using the obtained single-crystal elasticity, we have
calculated the azimuthal compressional wave anisotropy $[A_P = (V_{Pmax} - V_{Pmin})/ V_{Pave}]$ and
the shear-wave splitting $[A_{SPO} = (V_{S2} - V_{S1})/ V_{Save}]$ of ice-VII at high pressures and 300
K (Figure S6). Both $A_P$ and $A_{SPO}$ are much greater than those of mantle minerals (e.g.
Li et al., 2016; Mao et al., 2015; Mao et al., 2012; Murakami et al., 2007; Sinogeikin
et al., 2003). In contrast to silicates, elevating pressure leads to an increase in $A_P$ and
$A_S^{PO}$ (Figure S5). $A_P$ of ice-VII increases from 18.1% at 2.8 GPa to 26.9% at 53 GPa, while $A_S^{PO}$ increases from 41% to 65.8%. Due to the dipole ordering between 10 and 20 GPa, $A_P$ of ice-VII exhibits a weak softening at this pressure range, while a sudden increase was observed in $A_S^{PO}$ (Loubeyre et al., 1999). The evolution of ice-VII to the pre-transitional state also cause a weak anomalous change in $A_P$ and $A_S^{PO}$ between 42 and 53 GPa.

5. Implications

The mantle of some icy giants and satellites, such as Uranus, Neptune and Titan, is expected to have an ammonia to water volume ratio of 15:85 (Cavazzoni et al., 1999; Guillot, 2005). After the dehydration of ammonia-water completed above 4 GPa, the mantle of ice giants and satellites is estimated to contain ~80% H$_2$O-ice and ~20% AHH in volume ratio (Wilson et al., 2012). H$_2$O-ice is thus the dominant phase in the mantle of ice giants and satellites. Of particular importance is that, although AHH from the dehydration of ammonia-water mixture is normally polycrystalline, ice-VII always forms one nice single-crystal, regardless whether the starting composition is AMH, ADH, or ATH. Ice-VII exhibits anomalous large velocity anisotropies with increasing pressure. Here we evaluate the variations in the sound velocity of the AHH-ice-VII mixture due to the potential lattice preferred orientation of ice-VII in the mantle of ice giants and satellites.

Considering 20% of AHH and 80% of ice-VII in the mantle of ice giants and satellites, we have further modeled the velocity variation of AHH-ice-VII mixture up to 53 GPa at 300 K with considering the potential anisotropy of ice-VII at high pressures (Cavazzoni et al., 1999; Guillot, 2005). We focus on $V_P$ here because of...
lacking the experimental constraints on $V_S$ of AHH. Without the density of AHH at high pressures, $V_P$ in the mantle ice giants and satellites was calculated by averaging the velocities of AHH and ice-VII in a 1:4 volume ratio, which represents a first order estimation on the velocity profiles of the ice giants and satellites. Our modeling has shown that the difference in $V_P$ among AHH, ice VII and AHH-ice VII mixture is small below 7 GPa at 300 K (Figure 7). Yet elevating pressure dramatically increases the $V_P$ of AHH above 7 GPa. The difference in $V_P$ between AHH and ice-VII is 1% at 10 GPa and increases to 5% at 30 GPa (Figure 7). Addition of AHH thus can effectively increase $V_P$ of the AHH-ice mixture. Moreover, our modeling with 20% of AHH and 80% ice-VII in volume ratio in the mantle of ice giants has shown a non-linear increase of $V_P$ with pressure. The pressure dependence of $V_P$ dramatically decreases when ice VII in the AHH-ice VII mixture evolves to its pre-transitional state. The presence of the pre-transitional state ice-VII also causes a weak softening in the $V_P$ of the AHH-ice-VII mixture between 42 and 53 GPa (Figure 7). Considering the potential lattice preferred orientation of ice VII, we have calculated the maximum and minimum $V_P$ of the AHH-ice-VII mixture in the mantle of ice giants and satellite are shown in Figure 7. The difference in the maximum and minimum $V_P$ of the AHH-ice-VII mixture is 16.8% at 10 GPa and increases to 24.2% at 50 GPa.

In summary, we have investigated the phase stability and elastic properties of ammonia hydrate using Raman spectroscopy and Brillouin scattering up to 53 GPa and 300 K. Our Raman measurements have shown that any ammonia hydrate with a H$_2$O to NH$_3$ ratio greater than 0.5 will start to dehydrate at 2.1-2.2 GPa. The dehydration can cause the formation of ice-VII coexisting with the residual liquid between 2 and 4 GPa. The gradual precipitation of ice-VII also leads to an increase in
the concentration of NH$_3$ in the residual liquid. Yet the variation in the concentration of NH$_3$ does not cause any notable change in the velocity of the liquid phase. The residual liquid will transform to the solid AHH-II phase at ~4 GPa, leading to a 28% jump in $V_p$. Further Raman and Brillouin measurements have shown that solid AHH will coexist with ice-VII up to at least 53 GPa at 300 K. Although a change in the OH-stretching modes of AHH was observed at ~18 GPa which may be related to the AHH-II to AHH-DMA phase transition, we did not observe any anomalous variation in $V_p$ of AHH up to 30 GPa at 300 K (Ma et al., 2012a; Wilson et al., 2015).

Considering the mantle of a few ice giants with 10-15 vol.% NH$_3$, AHH should thus be the dominant form of ammonia hydrate coexisting with H$_2$O-ice in the mantle of these ice giants (Cavazzoni et al., 1999; Guillot, 2005).

It is interesting to note that ice-VII precipitated from the ammonia-water mixture always forms a nice single-crystal. It allows us to provide the constraints on the single-crystal elasticity of ice-VII up to 53 GPa and 300 K. Although $C_{12}$ of ice-VII nearly equals $C_{44}$ below 42 GPa within experimental uncertainties, the dipole ordering based on the Ising model causes $C_{12}$ to derivate from $C_{44}$ at 11.4 and 14.6 GPa (Loubeyre et al., 1999). Another interesting feature for the elasticity of ice-VII is the unusual softening of $C_{11}$, $C_{12}$, $K_S$ and $V_p$ together with the abnormal increase in $C_{44}$ between 42 and 53 GPa. The observed anomalous change in the elasticity between 42 and 53 GPa should be caused by the change of ice-VII to its pre-transitional state. Yet no abnormal variation with pressure was observed in both $G$ and $V_S$ because the softening of $C_{12}$ and $C_{11}$ between 42 and 53 GPa is compensated by the stiffening of $C_{44}$. In contrast to most silicates in the Earth, ice-VII exhibits a dramatic increase in the velocity anisotropy with increasing pressure. We further estimated the variation of
$V_p$ for the AHH-ice-VII mixture with a 1:4 volume ratio due to the potential lattice preferred orientations of ice-VII at high pressures. The difference between maximum and minimum $V_p$ of the AHH-ice-VII mixture reaches 24.2% at 53 GPa and 300 K. Future studies are expected to investigate the influence of temperature on the phase diagram and the potential anisotropy of ammonia hydrate and provide new insights on the structure of the ice giants and satellites.

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Reference


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**Figure Caption**

**Figure 1.** Representative Raman spectra and sample photos of ammonia hydrate. (a) AMH; (b) ADH; (c) ATH. Region A is related to the residual liquid after the precipitation of ice-VII from the ammonia hydrate which finally forms to AHH. Region B corresponds to the crystallized ice-VII.

**Figure 2.** Raman modes of ammonia hydrate at high pressures in region A(see Figure 1). (a) AMH; (b) ADH; (c) ATH. Dashed grey lines show the dehydration of ammonia hydrate, formation of solid AHH, and the potential AHH-II to AHH-DMA phase transition, respectively.

**Figure 3.** Raman modes of ice-VII. Solid circles: ice-VII formed from the dehydration of AMH (this study); open circles: ice-VII from pure H$_2$O (this study); blue line: ice-VII in Hsieh and Chien (2015).
Figure 4. Phase diagram of ammonia hydrate. Orange: liquid ammonia hydrate with varying NH$_3$ to H$_2$O ratio; red: left liquid ammonia hydrate after the precipitation of ice-VII; blue: AHH; green: ice-VII.

Figure 5. $V_p$ of ammonia hydrate at high pressures and 300 K in region A (see Figure 1). Green circles: liquid AMH; blue circles: liquid ammonia hydrate in the ration between AMH and AHH; red region: the polycrystalline of AHH with the upper and lower bounds of velocity; open orange circles: ADH at 296 K (Ma et al., 2012b); open pink circles: ammonia at 297 K (Li et al., 2009).

Figure 6. Elastic moduli of ice-VII at high pressures. (a) Single-crystal elasticity of ice-VII. Green: $C_{11}$; blue: $C_{12}$; red: $C_{44}$; solid circles: this study; open circles: Shimizu et al. (1995); (b) Bulk and shear moduli of ice-VII. Red: bulk modulus, $K_S$; blue: shear modulus, $G$; solid lines: our fitting results; dashed lines: anomalous change of the elastic moduli with pressure; open circles: single-crystal elasticity of ice-VII from Shimizu et al. (1995).

Figure 7. Modeled $V_p$ of the AHH-ice-VII mixture at high pressures and 300 K. Red line: ice-VII; blue line: AHH; black line: AHH-ice-VII mixture in a 1:4 in volume ratio; grey line: upper and lower bound of AHH-ice-VII mixture.
Figure 1

- **a. NH₃·H₂O**
  - Point A:
    - 22.9 GPa
    - 16.9 GPa
    - 10.1 GPa
    - 4 GPa
    - 3.6 GPa
    - 0.7 GPa
  - Point B:
    - 14.9 GPa
    - 11.4 GPa
    - 9.2 GPa
    - 6.4 GPa
    - 4.6 GPa
    - 2.2 GPa

- **b. NH₃·2H₂O**
  - Point A:
    - 15.5 GPa
    - 12 GPa
    - 7.3 GPa
    - 4.6 GPa
    - 3.9 GPa
    - 0.5 GPa
  - Point B:
    - 18 GPa
    - 13.7 GPa
    - 9.8 GPa
    - 5.3 GPa
    - 3.9 GPa
    - 2.1 GPa

- **c. NH₃·3H₂O**
  - Point A:
    - 20.4 GPa
    - 12.9 GPa
    - 7.6 GPa
    - 4.1 GPa
    - 3.6 GPa
    - 0.5 GPa
  - Point B:
    - 22 GPa
    - 18 GPa
    - 12.9 GPa
    - 8.9 GPa
    - 6.4 GPa
    - 3.8 GPa

Wavenumber (cm⁻¹)

- **a. NH₃·H₂O**
- **b. NH₃·2H₂O**
- **c. NH₃·3H₂O**
Figure 2

(a) $\text{NH}_3 \cdot \text{H}_2\text{O}$

(b) $\text{NH}_3 \cdot 2\text{H}_2\text{O}$

(c) $\text{NH}_3 \cdot 3\text{H}_2\text{O}$
Figure 3
Figure 4
Figure 5
Figure 6

(a) Invariant elastic constants $C_{ij}$ (GPa) as a function of pressure (GPa).

(b) Elastic moduli $K_S$ and $G$ (GPa) as a function of pressure (GPa).

Solid circles: This study
Open circles: Shimizu, 1995