Review

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Salt- and gas-filled ices under planetary conditions

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In recent years, evidence has emerged that solid water can contain substantial amounts of guest species, such as small gas molecules—in gas hydrate structures—or ions—in salty ice structures—and that these 'filled' ice structures can be stable under pressures of tens of Gigapascals and temperatures of hundreds of Kelvins. The inclusion of guest species can strongly modify the density, vibrational, diffusive and conductivity properties of ice under high pressure, and promote novel exotic properties. In this review, we discuss our experimental findings and molecular dynamics simulation results on the structures formed by salt- and gas-filled ices, their unusual properties, and the unexpected dynamical phenomena observed under pressure and temperature conditions relevant for planetary interiors modelling.

This article is part of the theme issue 'The physics and chemistry of ice: scaffolding across scales, from the viability of life to the formation of planets'.

1. Introduction

From comets' tails to icy planets' interiors, water in the Universe experiences an incredibly broad range of pressure and temperature conditions where it can fully disclose its uniqueness and show physical and chemical properties very different from those observed on Earth [1].

Most of the water on Earth actually exists in the form of salty water and/or contains gas species dissolved

in it, and it has now become evident from space mission data that this is also true for water in the solar system [1]. As examples: chemical analysis of the geysers emanating from the south pole of Enceladus by the Cassini space probe indicates a water salinity close to what is found on Earth, while the weak magnetic moment of Europa confirms the likelihood of a salty water ocean under the surface, as it provides the necessary electrically conductive layer in this moon [2]. Observation of sporadic methane release in the atmosphere on Mars has been related to the destabilization of methane clathrate hydrates at depth [3], and the methane observed in comets' tails is thought to derive from the destabilization of clathrate hydrate layers in their nuclei during their approach to perihelion [4].

In recent years, evidence has emerged that solid water can contain a substantial amount of a variety of guest species, such as small gas molecules (in gas hydrate structures) [5–14] or ions (in salty ice structures) [15–19], and that these 'filled' ice structures can be stable down to pressures of several Gigapascals (GPa) and temperatures of hundreds of Kelvins (K). The inclusion of guest species can strongly modify the density, the vibrational, thermal and ionic conductivity properties of ice under high pressure, and possibly promote novel properties, such as the predicted plasticity—a state where water molecules are held tightly in an ordered structure but freely rotate as in the liquid state [20], or superionicity—an exotic state of water in which the oxygens sit in their crystallographic positions while the protons delocalize and diffuse, giving rise to a protonic conductor [21]. The existence of ice phases highly loaded in guest species in extra-terrestrial bodies might thus challenge our present description of their physics, essentially based on the assumption of the properties of pure ice under high pressure. Nonetheless, the exploration of the phase diagram and properties of salt- and gas-filled ices still lags far behind that of pure ice.

In particular, the high-pressure phase diagrams of salty ices were almost unknown before our studies, as the common belief was that freezing water would almost entirely transform the salt into brine, as observed at ambient pressure [22]. This view was challenged almost 10 years ago, by the discovery of a high-pressure ice phase based on the ice VII lattice [16] including Li and Cl ions in the large fraction of one ion pair for each six water molecules ($R = \text{water molecules/ion pairs} = 6$) and showing structural and physical properties different from those of pure ice. Subsequently, LiBr and NaCl [18,19] have also been shown to form salty ice crystals under high pressure for R values close to their eutectic composition.

It is noteworthy that these *salt-filled* ice crystals show some structural similarity with the already known *filled* or *stuffed ices* [5–8], i.e. *gas-filled* ice structures formed at high pressure, where the gas molecules occupy interstitial voids in the ice skeleton.

Gas hydrates form each time water and hydrophobic gas molecules are in contact under high pressure and low-temperature conditions. For pressures lower than approximately 1 GPa, they adopt clathrate crystalline structures: hydrogen-bonded H_2O frameworks (cages), structurally similar to fullerenes, encage the guest gas molecules. Gas clathrate hydrates (also called 'ice clathrates') attracted a great deal of attention in recent years for (i) their role as a hindrance to the natural gas industry, (ii) their potential as an energy resource and (iii) their promising technological applications for gas storage and transportation, gas separation and desalination of seawater. For these reasons, gas hydrates, and methane hydrate in particular, have been widely studied in the relatively modest pressure range (0–1 GPa).

Until recently the expectation—based mainly on calculations—was that all gas clathrate hydrates would dissociate into ice and gas upon application of relatively modest pressures (approx. 1 GPa). However, over the past 15 years, new experimental studies have shown [5–8] that this view was incorrect. All the systems so far studied, with the single exception of Xe clathrate hydrate, undergo structural rearrangements to other, new types of hydrate structures (called 'filled ices') where the gas molecules occupying the channels of ice lattices isomorph to low-pressure phases of ice, which are stabilized at high pressure due to the presence of the guest gas molecules.

However, while *gas-filled* ices are stable structures which form by compression of ice clathrates [5], i.e. crystalline non-stoichiometric solids, *salt-filled* ices are likely metastable phases, obtained

Figure 1. (a) Observation of salt hydrates formation when cooling a NaCl water solution. (b) Snapshot of simulations from [22] showing solute expulsion from the forming ice Ih lattice while cooling an aqueous solution.

by crystallization upon temperature annealing of amorphous water–salt solutions at high pressure [16–19].

The first part of this review will describe our recent results on the structures and properties of LiCl, LiBr and NaCl ices under pressure, while the second part will report our recent results on new unexpected phenomena observed in CH₄ ice clathrates and filled ices under high pressure.

2. Salty ice structures and properties

Frozen water is normally unable to incorporate large amounts of salt (figure 1). This property is important for our climate, because, when seawater freezes, a solution of higher salinity—the so-called brine—is expelled. Since the brine has a higher density than seawater, it sinks and drives oceanic circulations in the polar region. The inability of ice to incorporate ions is not exclusive to the ordinary ice Ih phase, but applies to all the low-pressure phases. Based on this observation, made at ambient pressure, the presence of salts dissolved in water was always disregarded when dealing with its solid phase.

A few monohydrates and di-hydrates of simple salts were known to exist in nature and be stable under pressure, such as LiClH₂O, LiBrH₂O, LiH₂O, (NaCl)₂H₂O, (NaBr)₂H₂O, (NaI)₂H₂O and (LiI)₂H₂O. However, these hydrates are structurally unrelated to any form of pure ice, as the known ice phases tend to expulse ions from their lattice when they nucleate from a liquid salt–water solution. We have found that the situation is strikingly different when salt hydrates are obtained by temperature-annealing under high-pressure amorphous salty-ices obtained by fast freezing the eutectic salt–water solutions [16–19]. This route (figure 2) indeed leads to the crystallization of salt-filled ice phases similar to the high-pressure phases of ice, though showing a higher degree of rotational disorder for the water molecules [19] which indeed incorporate the ions. Depending on the size of the incorporated ion, it can occupy either an interstitial—as in the case of Li⁺ and Mg⁺ ions—or a substitutional position—as for Cl[−] and Br[−]—in the ice structure. We recall that the ion sizes of Li⁺ and Mg⁺⁺ are 0.9 and 0.86 Angstrom, respectively, while Cl[−], Br[−], and Na⁺ have ionic sizes of 1, 1.14, and 1.16 Angstrom.

The question then arises as to what are the properties of these salty ices under pressure in the GPa range, and relatively modest temperatures typically between 100 and 700 K, relevant for icy moons in our solar systems and beyond, under the extreme conditions encountered in larger icy bodies. We have characterized them by using neutron and X-ray diffraction techniques under pressure, coupled with Raman spectroscopy and molecular dynamics simulations, both classical and *ab initio* [16–19,23–29].

Figure 2. Scheme of the thermodynamic p-T path followed to crystallize salty ice VII from a $\text{LiCl} \cdot 6\text{D}_2\text{O}$ salty solution [16] superimposed to the p-T phase diagram of pure ice phases. The shadowed region is the one where amorphous salty ices have been observed.

Contrarily to their crystalline phases, salty aqueous solutions have been widely investigated, particularly in the undercooled regime and up to modest pressures (0.2–0.3 GPa) [30–34], in order to derive hints on the peculiar behaviour of water in the *no man's land*—the region of the phase diagram of water below the homogeneous nucleation temperature of ice and above the crystallization temperature of amorphous ice [35]. The addition of salts to water indeed favours undercooling and promotes amorphization [30]. When extrapolated to this experimentally impenetrable region, several of the thermodynamic properties of water seem to diverge. This observation has led to various theoretical models [36] to describe undercooled water, between them the hypothesis of the existence of a second critical point, marking the end limit of a separation line between a low-density and a high-density liquid, which would be the liquid proxies of the observed low-density (LDA) and high-density amorphous (HDA) states of water. Unfortunately, due to the extremely fast crystallization in the *no man's land* this hypothesis could be tested only against molecular dynamics simulations.

The first point to stress is that the low-density amorphous phase of ice, as its crystalline counterpart, is normally also unable to incorporate significant amount of salts into its network. The open and locally ordered structure of LDA is perturbed and hindered by the presence of ions [24].

Salty-LDA forms can only be produced at high dilution rates by hyper-fast cooling (greater than 10^7 K s^{-1}) the solution, in order to force the system to freeze into an amorphous state without expelling the ions [25].

If the salt concentration is high enough ($R < 12$), solid HDA phases can be produced either by fast quenching [26,28] or by simply cooling the salty solution [23]. The electrostrictive effect provided by the ions on water molecules [26,28] indeed favours a more compact organization of the molecules in solution, with respect to pure water, and this independently of the size of the cation. This compact spatial organization is retained in the glassy state obtained by cooling the solution [23,26], provided that a structural relaxation of the liquid during the glass formation is enabled by the use of standard cooling rates. This produces what will be called in the following salty-HDA solids. Concentrate salty solutions around the salt–water eutectic composition ($R = 6$ for LiCl, $R = 5.6$ for LiBr, $R = 10.2$ for NaCl) are indeed good glass formers [37,38]. In spite of the

Figure 3. Diffraction patterns of amorphous salty ices measured at ambient pressure by neutron diffraction. From bottom up: NaCl · 10.2D₂O pattern measured on D20 (ILL), LiBr · 5.6D₂O pattern measured at PLANET (J-PARC, Japan), LiCl · 6D₂O measured on PEARL (ISIS, U.K.), pure water e-HDA from [39] and pure LDA from [40].

Figure 4. Metastable phase diagram of salty ice as suggested by our experiments. The snapshots of simulation show the most common configurations in the two polymorphs. Cl (green), Li (orange), O (red) and H (white).

high amount of dissolved salt, these salty-HDA solids are homogeneous and structurally compact forms with a structure very similar to that of the equilibrated high-density amorphous phase of pure water (e-HDA) [35] (figure 3).

When temperature-annealed for pressures above 2 GPa (figure 4)—from 80 K to 150 K—LiCl and LiBr eutectic solutions evolve towards new distinct very high-density (VHDA) phases [35]. The transition phenomenology is similar to that observed for the LDA to HDA transition in pure water [28]. Salty-VHDA retains a markedly different microscopic structure with respect to salty-HDA: the first peak of its structure factor is shifted from a wavevector transfer $q = 2.10 \text{ \AA}^{-1}$ (figure 3) to $q = 2.28 \text{ \AA}^{-1}$ [35] and its intensity is substantially lower, while the second peak evolves in the opposite direction, i.e. a displacement to lower q -values is observed. A simple description of the observed transition can be obtained by looking at the Li-X (with $X = \text{O, Cl}$) pair distribution function, as this pair function shows a very well-defined first neighbours shell around the Li^+ ion:

the system undergoes a change between a ‘mainly fourfold’ coordination around the Li^+ ion in the salty-HDA state to a ‘mainly sixfold’ coordination in the salty-VHDA state (figure 4).

The case of NaCl water solution close to its eutectic composition ($R = 10.2$) is rather different [26]: due to the larger size of the cation, the ambient-pressure glass is already octahedrally coordinated around the Na ion, the structure factor of the system changes continuously both upon isothermal compression at 140 K, and upon annealing from 80 K to 160 K under high pressure. Densification, in this case, occurs first by compression of the octahedral coordination shells of Na^+ ions, followed by a progressive distortion of the octahedra at pressures above 2 GPa and a smooth increase of the average coordination, which becomes eightfold only above 8 GPa. This is in contrast to what was observed in LiCl and LiBr solutions where Li^+ tetrahedral coordination abruptly breaks up near 2 GPa, giving rise to a transition to a sixfold coordinated structure. This observation suggests that the phenomenon of polymorphism, observed in pure water and in aqueous LiX solutions, is not a general feature of electrolytic aqueous solutions, but is rather typical of the tetrahedrally coordinated systems.

For pure water, compression of its amorphous phases at a low temperature above 2 GPa results in crystallization of ice VIII [41]—the fully proton-ordered structure of ice. Conversely, all the salty solutions investigated so far can be compressed up to pressures above 10 GPa without undergoing crystallization at low T . This is a consequence of the augmented orientational disorder of the water molecules induced by the presence of salt: the electric field of the ions interacts strongly with the electric dipole moment of the water molecules and perturbs both the molecule orientation and the directional hydrogen bonding to its neighbours. This ultimately hinders the formation of a stable proton-ordered structure.

The discovery of the existence of salty ices under pressure was somewhat accidental: when warming up salty-VHDA produced by a $\text{LiCl} \cdot 6\text{D}_2\text{O}$ solution at approximately 4 GPa, we observed a continuous reduction of the diffraction peak width until a sudden crystallization occurred at 271 ± 1 K. Neutron diffraction unambiguously enabled us to assign this new crystalline structure to ice VII, i.e. the phase of pure ice that is expected to occur at this temperature and pressure [41] (see inset of figure 5). Ice VII crystallizes in space group $\text{Pn-}3\text{m}$ with O at $(1/4, 1/4, 1/4)$ and H at $(0.41, 0.41, 0.41)$ with site occupancy 0.5. This produces an average structure with oxygen on a body-centred-cubic (b.c.c.) lattice and twice as many H sites as hydrogen atoms available. The diffraction pattern clearly showed the so-called Huang diffuse scattering, characterized by tails under the main reflection peaks (figure 5). Such a phenomenon is produced by the scattering from the strain field of interstitials and, together with the evidence given below, is a fingerprint for incorporation of Li and Cl into the ice VII structure.

The Rietveld fit of the diffraction pattern (figure 5) revealed two main effects: firstly, the refined unit cell volume is 9% larger (up to 17% in the case of $\text{LiBr} \cdot 5.6\text{D}_2\text{O}$ solutions) than expected for pure ice VII at this pressure and temperature; secondly, unusually large displacement factors are found both for oxygen ($\langle x^2 \rangle^{1/2} = 0.34 \text{ \AA}$) and deuterium ($\langle x^2 \rangle^{1/2} = 0.35 \text{ \AA}$), an effect that cannot be attributed to thermal motion but must arise from large positional disorder.

Finally, upon cooling below 270 K, pure ice VII transforms into its proton-ordered form, ice VIII. This consists of two interpenetrating networks with H_2O dipoles pointing in well-defined opposite directions along [001]. Conversely, the salty ice shows a pattern strictly identical to the one collected at high temperatures down to 80 K. The observation of Huang scattering, the unusually strong attenuation of Bragg reflections, the expanded lattice parameters, and the non-recovery of the ordered phase VIII under cooling, conclusively suggest that the Li^- and Cl^+ ions are incorporated into the ice VII structure, rather than being expelled into grain boundaries.

The number of possible sites for Li^- and Cl^+ in the structure of ice VII is actually very limited. Published structural data for the salt hydrates $\text{LiCl} \cdot \text{H}_2\text{O}$ and $\text{LiBr} \cdot \text{H}_2\text{O}$ show that Li^+ always adopts an octahedral coordination. This is also true in its glassy VHDA phase, which acts here as a precursor of the salty ice VII crystal (figure 6).

As previously discussed, Li^+ adopts a sixfold coordination in the salty-VHDA phase, which thus favours the inclusion of the ion, upon crystallization, in the interstitial position located at the face centre of the unit cell of ice VII. Due to the similarity in molar volume between the Cl^- ion

Figure 5. Diffraction pattern of $\text{LiCl} \cdot 6\text{D}_2\text{O}$ at 4 GPa and 280 K. The line through the data (circles) is a Rietveld fit to the pattern based on the ice VII structure, and the difference plot is given below. Tick marks indicate positions of reflections, red stars the fitted reflections. The anomalously strong Debye–Waller factor is evident from their drop in intensity with q . The red arrow indicates the diffuse Huang scattering and the drawing on the left depicts the mechanism generating this diffuse intensity. The inset shows schematically the pressure–temperature path before crystallization superimposed to the phase diagram of pure water as well as schematic diagrams of ice phases VII and VIII. Red and grey spheres represent oxygen and hydrogen, respectively.

Figure 6. Li^+ ion in an octahedral configuration in the salty-VHDA solid (a) and in the salty ice VII crystal (b).

and a water molecule, the most likely positions of the anion within our proposed structure are the oxygen substitutional lattice sites preferentially in the vicinity of a Li^+ cation. Incorporation of Li^+ and Cl^- in the structure of ice VII following this model requires average local distortions of 0.2–0.3 Å, i.e. displacements in agreement with the measured Debye–Waller factor. The presence of Li^+ and Cl^- ions also prevents a long-range ordering of the molecular orientation of water, that is, a transition to the proton-ordered ice VIII when the sample is cooled. This is not surprising given the strong electrostatic interactions involved.

Interstitial incorporation was known to occur for small neutral molecules such as He [42] or H_2 [43], producing ‘stuffed ice’, but not for ionic species. We expect that the incorporation of ions significantly modifies the properties of ice VII. For example, owing to its interstitial position, the Li^+ cation is thought to be able to jump from site to site, resulting in likely strong ionic conduction.

Further neutron diffraction and molecular simulation results on highly concentrated LiCl and LiBr ices—produced by crystallization under pressure of amorphous solutions—indicated that

Figure 7. Probability density distribution of the electric dipole moment of H_2O in pure ice VII (c), and $\text{LiCl} \cdot 6\text{H}_2\text{O}$ (d) derived from molecular dynamics simulations [18]. The distribution was normalized to give an integrated probability equal to one. A sketch of a typical instantaneous configuration in pure ice VII (a) and in $\text{LiCl} \cdot 6\text{H}_2\text{O}$ (b) is given with hydrogen bonds indicated as dashed lines and the non-bonding (anti-tetrahedral) directions as dotted lines. Li^+ and Cl^- ions are yellow and green spheres, respectively.

the ionic species are trapped inside a strongly expanded ice VII-like structure with random electric dipole orientation [18] (figure 7). Molecular dynamics simulations showed that while pure ice VII is characterized by molecular dipoles sharply aligned along [100] and equivalent directions, $\text{LiCl} \cdot 6\text{D}_2\text{O}$ and $\text{LiBr} \cdot 5.6\text{D}_2\text{O}$ ices have an almost isotropic dipole orientation (figure 7). The salty ice VII-like structures have thus completely disordered molecular orientations, which also means that a large fraction of hydrogen bonds is broken and that the ice rules are violated. This distinguishes salty ices from the orientational disorder present in most of the pure ice phases where the ice rules are indeed conserved.

The crystallization of salty ices can thus be classified as ‘partial’ since it concerns mainly the three translational degrees of freedom, whereas the three rotational degrees of freedom remain uniformly random even though frozen, in contrast to a plastic crystal. Contrarily to high-pressure ice phases, these structures cannot be recovered to ambient pressure and low temperatures. When the pressure is released, they transform back to a glass with a structure different from the initial one, and likely recover a fraction of broken hydrogen bonds [18].

Concerning the possibility of incorporation of more relevant—due to their abundance in nature—salts such as NaCl , experiments are still controversial.

First experimental evidence for the incorporation of small amounts (2 mol%) of NaCl into ice VII by compression of the salty liquid has indeed been proposed in [15,44], but the suggested lattice contraction under salt inclusion seems unrealistic. Our neutron diffraction experiments on dilute NaCl and LiCl solutions indicate that the salt is indeed expelled if the solution is compressed at ambient temperature [19]. Having observed the crystallization of LiCl and LiBr -ice VII from the amorphous precursors by annealing them under pressure, it is also conceivable that

Figure 8. Simulations [19] showing Na⁺ ion in a sixfold configuration in the salty amorphous at ambient pressure (a), in an eightfold configuration in the salty-VHDA solid (b) and in the salty ice VII crystal obtained annealing under pressure (c).

ice VII with a very high salt content could be produced starting from an amorphous NaCl-water mixture, following the same thermodynamic path described in figure 2.

We tried this route by temperature-annealing fast quenched [26,28] NaCl · R D₂O amorphous solutions with R ranging from 10 to 12, i.e. close to the eutectic composition, at pressures between 3.5 and 4.2 GPa. As in the case of LiCl and LiBr solutions, we observed ice VII crystallization at about $270 \text{ K} \pm 5 \text{ K}$ [19]. The lattice of this putative NaCl-filled ice VII crystal showed a volume expansion of only 1.2%, and much smaller distortions (the Debye–Waller factor is indeed similar to that of pure ice VII) with respect to LiCl- and LiBr-filled ice VII. Also, on cooling, we recovered a mixture of expanded ice VII and pure ice VIII phase, which rather indicates that the incorporation was not complete.

Using the same argument employed to unravel the LiCl-filled ice VII structure, based essentially on the known structure of the amorphous precursor and on the measured lattice expansion, we believe that the Na⁺ ion might be included in the ice VII lattice by occupying a substitutional site, as Cl⁻, and thus occupying the centre of the bcc cube and not one of its faces as Li⁺ (figure 8). This would reduce the lattice expansion and the distortion of the water molecules' position with respect to an interstitial position, following the experimental observation. However, this inclusion mechanism probably requires higher pressures than those applied in our neutron scattering experiments [19], in order to maximize the number of eightfold coordinated ions in the amorphous precursor, which most likely gives rise to crystallization into the substitutional ice VII. Further neutron scattering experiments are needed to corroborate this hypothesis, and the stability of the proposed Na⁺ and Cl⁻ substitutional structure needs to be tested by *ab initio* simulations.

The existence of NaCl ice VII was compatible with our Raman spectroscopy experiments in diamond anvil cell (DAC) devoted to probing the effects of salts on the hydrogen-bond symmetrization in ice at very high pressure [17,27].

We indeed investigated, by Raman spectroscopy up to Megabar (Mbar) pressures and *ab initio* simulations, how the transformation of ice VII into ice X is affected by the presence of salt inclusions in the ice lattice. In ice VII, the hydrogen bonds are characterized by a pronounced double-well proton transfer potential. Upon reducing the distance between donor and acceptor oxygens, the proton potential degenerates into a single-well potential, giving rise to a *symmetric* or *centred* hydrogen bond, where hydrogen atoms are located midway between two neighbouring oxygen atoms. This new phase is called ice X. The transition between ice VII and ice X is a prototypical case of quantum-driven phenomenon, as it can be described as a quantum delocalization of protons in the middle of O–O distances. This transition has been observed with different spectroscopic techniques for pure ice [45,46] to occur at about 60 GPa, i.e. at pressures experienced in the interior of large ice bodies in the universe, such as Saturn and Neptune, where non-molecular ice is thought to be the most abundant phase of water.

We investigated salty ice VII samples LiCl · RH₂O, at different salt concentrations—namely $R = 6, 12, 30$ and 50 —exploiting the high vitrification ability of LiCl water solution in order to prepare the amorphous precursors of salty ice VII at tailored salt concentrations [17]. In particular,

$R = 6$ aqueous solutions were directly loaded into high-pressure chambers of 30–40 micrometres in diameter and cooled at standard cooling rates, while $R = 12$ solutions were cooled by quenching (10 K s^{-1}) the aqueous solution in a nitrogen bath and then cryo-loading in the DAC. Finally, $R = 30$ and $R = 50$ LiCl aqueous solutions were loaded in the cell at ambient temperature into gold-coated high-pressure chambers of 10 mm in diameter, compressed to 2–3 GPa, warmed at 673 K at a final pressure of 5 GPa in order to achieve the liquid state, and then fast quenched (cooling rate $> 10^2 \text{ K s}^{-1}$) to 77 K by directly immersing the DAC into liquid nitrogen in order to produce the amorphous precursor. All the samples were then compressed to 5 GPa at nitrogen temperature, and temperature annealed at this pressure, in order to induce crystallization of salty ice VII. The typical Raman signature of this crystallization was the sharp narrowing and splitting into three bands of the OH stretching modes in the frequency range $3100\text{--}3700 \text{ cm}^{-1}$, as reported in [17]. As in the case of pure ice VII, the three OH stretching modes—assigned to the ν_1 (A_{1g}), ν_3 (E_g) and ν_1 (B_{1g}) modes in order of increasing frequency—appear distinct in the Raman spectra of the crystal, even if broadened by the increased disorder in the structure introduced by the salt. A similar criterion was used—in a following experiment—to monitor the inclusion of NaCl in ice VII by fast quenching a droplet of a NaCl·53H₂O solution (of 5 mm in diameter) with cooling rates of the order of $10\text{--}100 \text{ K s}^{-1}$. Also in this case crystallization into ice VII was observed when warming up the amorphous precursor at pressures above 4.8 GPa [27].

As in pure ice VII [45,46], we observed a softening of the OH stretching modes with increasing pressure, indicating the approach of a displacive phase transition [47]. In particular, the low-frequency ν_1 (A_{1g}) band has the strongest softening in pure water and this has been directly linked to the appearance of the ice VII to ice X transition at higher pressures. In both LiCl- and NaCl-filled ice VII, the softening of these bands was strongly reduced with respect to pure ice [17,27].

In pure ice VII, further increase of pressure to about 75 GPa results in the appearance of a new, narrow band in the low-frequency spectrum at about 900 cm^{-1} , attributed to the OO stretching mode in the symmetric ice X phase [46]. The frequency of this new excitation increases with pressure and the corresponding peak is the only first-order excitation in pure H₂O at these pressures, due to symmetry restrictions. As shown in [17,27], the appearance of this band is observed also in salty ice VII but pushed to higher and higher pressure as the salt content increases (namely at about 90, 100 GPa and 120 GPa for LiCl·RH₂O with $R = 50, 30$ and 12 , respectively, and to 87 GPa for NaCl·53H₂O solutions).

Thus, even a very small salt concentration ($R = 50$) shifts the ice VII to X transition by 10–15 GPa, and this independently from the cation and from its actual position, whether interstitial or substitutional. This indicates that the shift of the transition pressure does not depend, within our statistical uncertainty, on the type or size of the ionic impurity introduced in ice and that this phenomenon cannot be explained simply as an effect of the ion-induced local distortion of the neighbouring ice structure, and consequent perturbation of the motion of hydrogen atoms nearby [27].

A deeper atomic-level analysis—obtained by the help of *ab initio* molecular dynamics simulations [27] including nuclear quantum effects using a thermal quantum bath approximation—indicates that the incorporation of salt in high-pressure ice generates a long-range electric field that affects all the protons in the system, beyond the local distortion. This electric field modifies the potential landscape around the protons, making it asymmetric instead of symmetric as in pure ice (figure 9). Even a small asymmetry is able to localize the hydrogen nuclei and to largely suppress tunnelling along the O–O direction, shifting the transition to salty ice X to higher pressures. This explains why the disappearance of nuclear quantum effects on the protons occurs even at rather low salt concentrations [27].

Finally, we want to stress that the observed salty ice structures seem to be stable up to very high pressures, as the changes observed in the Raman spectra are continuous up to the observed salty ice VII to salty ice X transition, proportional to the initial salt content, and consistent with a gradual transformation of the salty ice VII crystal into the symmetric salty ice X phase.

Figure 9. Probability for the proton to be in the lowest well of the potential between two oxygen sites as a function of electric field intensity [27] (a) and sketch of the salty ice VII to salty ice X transition (b).

The stability of this phase under high temperature remains to be addressed. This is indeed a relevant point, as ice X is also thought to be the precursor for a superionic ice phase [21], which would manifest itself in the pressure range of ice X but at higher temperatures. This superionic phase is a non-molecular phase characterized by mobile delocalized hydrogen atoms moving in the oxygen lattice and giving rise to electrical conduction. This ice phase has been proposed to be responsible for the observed anomalous magnetic moment of Uranus and Neptune [48,49].

To conclude, we have explored the phase diagram of LiCl-, LiBr- and NaCl- water mixtures in a broad range of pressure and temperature conditions and we have characterized some of their anomalous structural and dynamical properties (figure 10). However, most regions of this phase diagram are only sketched and need to be investigated in further detail. Furthermore, the thermal and electrical conductivity properties of these salty ices urgently need to be explored, in order to understand the relevance of their existence for astrophysical and geodynamical models of planets.

3. New phenomena in ice clathrates and filled ices under high pressure

Gas hydrates are non-stoichiometric inclusion compounds that water spontaneously forms with a variety of more than 130 gas species (including common natural gases, hydrocarbon molecules, etc.) whenever sufficient pressure—a few tens MPa at most—and low-temperature conditions occur [5].

These compounds have crystalline water frameworks adopting clathrate structures in the relatively modest pressure range (0–1 GPa), the most common ones being the primitive cubic clathrate structure I (sI) and the face-centred cubic clathrate structure II (sII). Those structures differ by the type and number of polyhedral cages forming their unit cells, as shown in figure 11. The unit cell of sI contains 46 water molecules forming two ‘small’ pentagonal dodecahedra (average diameter of 7.9 Å) and six ‘large’ tetrakaidecahedra made of 12 pentagons and two hexagons (average diameter of 8.66 Å). The unit cell of sII contains 136 water molecules forming 16 small pentagonal dodecahedra and eight ‘large’ hexakaidecahedra made of 12 pentagons and four hexagons (average diameter of 9.46 Å) [5]. For medium-sized gas molecules such as methane, typically approximately 80% of the small cages and 95% of the large cages contain a gas molecule, implying water-to-gas molar ratios of about 6 to 1 for both sI and sII.

Figure 10. Pressure–temperature phase diagram of LiCl ice as sketched from our neutron diffraction experiments and molecular dynamics simulations [16–19,23–29]. Specific thermodynamics paths have been followed for $R = 6$ and 13 solutions (1) and for $R = 30$ and 50 solutions (2) in order to first produce the amorphous precursor embedding the salt and then crystallize salty ice under pressure. The shadowed part is the region of existence of the polyamorphic salty-HDA and salty-VHDA phases [23].

Figure 11. Crystal unit cells of clathrate sI and sII, adapted from [13]. The vertices of the polyhedra correspond to oxygen atoms and the edges correspond to hydrogen bonds. Different types of polyhedra are plotted with different colours.

Being constituted of 85% hydrogen-bonded water molecules, gas clathrate hydrates naturally share most of their properties with ice Ih. Yield strength, thermal expansivity and thermal conductivity are well-known exceptions. Nevertheless, the amount of gas contained in ice clathrates can be regarded as being remarkable when compared to the typical solubilities of (nonpolar) gases in water. As an example, solubility of CH_4 in water at ambient conditions is only 2.48×10^{-5} mole fraction [5], which corresponds to a molar ratio of about 40 000 to 1. Furthermore, clathrate hydrates are very dense in guest molecules also in comparison to the pure gas phases—for example, one volume of methane clathrate hydrate may contain the same amount of gas as 180 volumes of pure methane at standard conditions or as one volume of pure methane at 18 MPa and 273 K.

Compared to other inclusion compounds, gas hydrates are peculiar in at least two respects. First, they are both crystalline and non-stoichiometric—a minority of the cages can be empty and multiple cage occupations are possible for sufficiently small guests [5]. Second, their stability relies on the combination of two different types of molecular bonding—the water molecules form hydrogen bonds between them while Van der Waals interactions exist between water and the guests and between the guests.

As a general rule, gas molecules with a van der Waals diameter comprised between 4.3 and 6.0 Å (e.g. methane and carbon dioxide) prefer to form sI while gas molecules with diameters below 4.3 Å (e.g. H₂, N₂ and CO) or comprised between 6.0 and 7.5 Å (e.g. propane and isobutene) prefer to form sII. However, in practice, many medium-sized guests can stabilize both sI and sII and structural metastabilities are ubiquitous in clathrate hydrate science. As examples, CO and N₂ clathrate hydrates have been observed to initially crystallize into sI and then gradually transform into sII over days or weeks [50,51]. CO₂ and CH₄ are sI-formers; however type II-like structure is transiently observed in the initial stages of their formation [52,53]. Moreover, sII has been reported to *persistently* coexist with sI in methane hydrate at room temperature and pressures of a fraction of GPa [54,55].

Naturally occurring on the ocean floor and in the permafrost, methane hydrates are expected to play a role in energy harvesting and in promising environmental technologies: more specifically, methane/carbon dioxide exchange in natural clathrate deposits appears to be a win-win approach for CH₄ recovery and CO₂ mitigation [9]. H₂ hydrates can reversibly store and release molecular hydrogen up to mass fractions of some per cent, thus appearing as a hydrogen storage system that could figure prominently in a hydrogen economy [10–12]. However, assessing the technological viability of such energy applications and implementing them requires a full understanding of the out-of-equilibrium phenomena involving clathrate hydrates—in which the dynamics of the gas molecule plays a crucial role—which is still missing.

(a) Methane diffusion at the interface of clathrate structures at moderately high pressure

While cage-to-cage hopping of methane through clathrate sI had been investigated in the literature and known to be very slow (on the microsecond timescale) [56,57], no information was available on the guest diffusion at grain boundaries, although this process must play a crucial role during out-of-equilibrium phenomena such as formation or decomposition of a clathrate structure, and gas exchange. We characterized the diffusion mechanism and timescale of methane molecules diffusing out of the clathrate structures as a function of temperature by quasi-elastic neutron scattering (QENS) measurements [13]. This was achieved by exploiting the possibility to stabilize by pressure the non-equilibrium sI-sII coexistence in methane clathrate for long enough times to perform QENS measurements.

The starting clathrate sI frame-deuterated (CH₄-D₂O) methane hydrate sample was prepared in a laboratory following a well-established procedure [56] and contained approximately one methane molecule every six water molecules. The sample was loaded into the clamp module of the Paris-Edinburgh pressure cell in a liquid nitrogen bath and compressed to 0.8 GPa at cold. After warming up to room temperature, the sample was found to contain a mixture of sI and sII (with about half as much sII as sI). We recorded QENS spectra of this sample at the constant temperature of 282 K and pressure of 0.8 GPa during 6 h. The amount of sI and sII was constant during this time. Then we continuously decreased the temperature to 200 K over 15 h—during which the amount of sI and sII remained approximately constant—to characterize the temperature dependence of the quasi-elastic signal at 0.8 GPa.

Analysis of the quasi-elastic signal deriving from the hydrogenated methane only—as the contribution from deuterated water is negligible—reveals mobility on the picosecond timescale involving a sizable fraction of the methane molecules in the sample (approximately one-third, as a rough estimation). The QENS signal was analysed using a Lorentzian function—corresponding to a three-dimensional diffusion model—and a two-dimensional diffusion model [63]. The fits obtained within the two models are indistinguishable in our spectra within the instrumental

Figure 12. (a) Temperature dependence of the measured translational diffusion coefficient of methane in the clathrate sI-sII sample at 0.8 GPa, as obtained in the three-dimensional and two-dimensional diffusion models. Arrhenius fits are shown as dashed lines. Estimated value for pure methane at the same pressure from the literature [58,59] is also reported. Reproduced from [13]. (b) Schematic suggestions for the three-dimensional and two-dimensional diffusion processes.

energy resolution and provide comparable translational diffusion coefficients, here reported in figure 12. The QENS signal shows a wavevector transfer dependence that corresponds to a non-confined translational random jump diffusion, so it must arise from methane molecules diffusing out of the clathrate structures.

The obtained diffusion coefficients are of the order of $10^{-4} \text{ cm}^2 \text{ s}^{-1}$, i.e. a factor of two to three higher than that expected for pure bulk fluid methane at comparable pressure and temperature (figure 12), and one order of magnitude higher than that of methane dissolved in water at low pressure [60]. This remarkably fast methane diffusion could be explained by the formation of methane nanobubbles in disordered regions of the sample, since the diffusion coefficient of methane inside these bubbles might be considerably different from the bulk fluid. Micro-nanobubbles formation during clathrate decomposition was suggested in the past [61,62] but remains debated. Alternatively, our findings could be ascribed to a hyper-diffusion phenomenon arising from the hydrophobic interaction of methane molecules with a peculiar layered structure of the sI and sII coexisting assemblies in the measured high-pressure sample [13]. In the first scenario, the fast methane diffusion would not be specific to the measured sI-sII sample and could be in principle a general feature of methane clathrate hydrate during many different out-of-equilibria processes, such as clathrate formation or decomposition, and gas exchange, and in general any process involving methane diffusing out of the clathrate structure. Insights from molecular dynamics simulations and new experiments are needed to shed light on this point.

The diffusion coefficients we reported in figure 12 are also 7–8 orders of magnitude higher than those previously reported for cage-to-cage hopping of methane through clathrate sI [56,57]. In the literature, the very slow cage-to-cage methane hopping process has often been taken into account in the modelling of the evolution of naturally existing methane clathrate layers. For example, in the estimation of the steady state of the clathrate layer which is believed to exist in the cryosphere of Mars, the timescale for cage-to-cage methane hopping has been compared to the clathrate formation and dissociation rates [3]. We suggested that the diffusion coefficient for methane at the interface of grains, which is much faster, should be also considered [13]. More experimental work would be required to estimate the diffusion coefficient over the geophysically relevant temperature–pressure ranges.

(b) Stability and structure of gas-filled ices under high pressure

The study of gas-filled ice structures under pressures of GPa and above is a relatively recent field. Loveday *et al.* [6] reported in 2001 the first observation of the orthorhombic methane-filled ice structure resembling ice Ih—known as ‘MH-III’—formed by the hydrate of methane when compressed above 2 GPa. Equivalent structures have afterwards been observed for the hydrates of argon, krypton and nitrogen, as reviewed in [8], and it became clear that the same gas hydrates that form clathrate structures at modest pressures commonly form filled ice structures when compressed to GPa pressures. Xe clathrate hydrate has been reported to decompose into ice and xenon upon compression to 2.9 GPa [64] and is the only known exception. On the other hand, the water–helium and water–hydrogen systems, which were known to form filled ice-structured hydrates in the GPa range since the late 1980s and early 1990s [42,43], more recently turned out to also form clathrate structures at lower pressures [65,66]. Helium hydrate forms a filled ice structure resembling ice II [42] and hydrogen hydrate forms two filled ice structures resembling ice II and ice Ic [43]. A third structure, which is unrelated to any stable phase of ice and is referred to as structure ‘C0’, has been recently found for hydrogen hydrate at pressures of a fraction of GPa [11,67,68]. The C0 structure was also observed for the carbon dioxide–water system [68]. Finally, a filled ice structure resembling ice II has been recognized for the hydrate of neon [69].

The study of these gas-filled ice structures is in principle relevant to the modelling of the interiors of the icy giants of our solar system and of other large bodies out of the solar system, where water and simple gas molecules are expected to coexist. However, the ranges of stability of these high-pressure filled ices, as well as their thermal, dynamical and proton conductivity properties, mostly remain to be established. As examples, Hirai *et al.* reported that Ar-filled ice decomposes into ice and argon when pressure is increased to 6.1 GPa [70], and, similarly, stated that the hydrates of krypton and nitrogen decompose at 5.5 and 3.8 GPa, respectively, but did not present either a reference or data to support this second statement [7]. Sasaki *et al.* [71,72] measured both krypton and nitrogen hydrates by Raman spectroscopy up to 5.2 GPa and 6.0 GPa, respectively, and did not observe decomposition into ice and gas. In addition, Loveday & Nelmes [8] stated having unpublished data indicating stability of nitrogen hydrate up to at least 30 GPa.

Hydrogen hydrate was found to be stable at least up to 77 GPa [73] and shows a structural transition from the filled ice Ic structure to an unsolved high-pressure phase at about 45 GPa [74]. The presence of pure hydrogen was clearly revealed in the Raman spectra of the samples of [73] above 20 GPa and interpreted by the authors as a stabilization mechanism for the hydrate structure: in response to the close arrangement imposed by the pressure increase, a fraction of the hydrogen molecules in the hydrate would be progressively extracted [73]. Nevertheless, a partial and progressive decomposition of the hydrate with increasing pressure cannot be excluded.

For methane hydrate, the group of Hirai reported a series of Raman spectroscopy and synchrotron X-ray diffraction data reaching a maximum pressure of 86 GPa in which no decomposition into ice and methane was observed [7,75–78]. Instead, progressive disappearance of some diffraction peaks and appearance of new peaks was observed in the diffraction patterns at 40–50 GPa, indicating existence of a slow transition from the filled ice Ih structure (MH-III) into a different structure [75–78]. The high-pressure structure, which would survive up to at least 86 GPa, could not be identified in [75–78]. Finally, the high pressure/high-temperature decomposition curve of methane hydrate up to 633 K and 40 GPa has been recently published [78].

We have addressed the problem of the stability of methane hydrate under very high pressure by performing Raman spectroscopy measurements up to 150 GPa [79], the highest pressure explored to date for gas hydrates. The CH₄–D₂O methane hydrate sample was loaded into a DAC in a liquid nitrogen bath and compressed to 3–4 GPa at cold. The closed cell was then warmed up from liquid nitrogen temperature to room temperature and the Raman spectroscopy measurements were carried out at room temperature. Figure 13 reports the Raman spectra of the sample measured at pressures between 36 and 150 GPa.

Figure 13. Raw experimental Raman spectra of $\text{CH}_4\text{-D}_2\text{O}$ methane hydrate (and excess ice) at room temperature and the indicated pressures between 36 and 150 GPa.

The reference Raman spectrum at 36 GPa in figure 13 contains peaks from different modes of the sample: the lattice mode at 450 cm^{-1} , the CH_4 rocking mode at 1600 cm^{-1} , the OD stretching modes at $1900\text{--}2100\text{ cm}^{-1}$ and the CH stretching modes at 3100 and 3250 cm^{-1} . Diamond first-order signal at 1400 cm^{-1} and second-order at $2200\text{--}2800\text{ cm}^{-1}$ are also visible in the spectrum. The lattice mode, the CH_4 rocking mode and CH stretching modes shift to higher frequencies as pressure increases; the OD stretching modes shift to smaller frequencies. The lattice mode loses intensity upon compression and is barely distinguishable above 50–60 GPa. Similarly, the CH_4 rocking mode broadens considerably upon compression above 40 GPa and has no detectable intensity above 50–60 GPa, and the two OD stretching modes lose intensity very sharply over the range between 35 and 45 GPa. On the other hand, the two CH stretching modes can be seen up to the maximum investigated pressure of 150 GPa; the pressure dependences of their frequencies are smooth over the pressure range 36–150 GPa and are well fitted by polynomial functions. Also, at all pressures the frequencies of the CH stretching modes clearly differ from those of pure methane as reported in [80,81], indicating that methane hydrate is stable at least up to 150 GPa, a pressure which is relevant for large planets such as Jupiter and Neptune, having methane and water among their main constituents. The post-MH-III structure will be published elsewhere [79].

In the following, we will focus our attention on the pressure range between 2 and 45 GPa in which methane hydrate forms the filled ice structure named MH-III [7,8,75–78]. MH-III was indexed as a body-centred orthorhombic structure with space group Imcm (a variation of the space group Imma , No. 74) [8]. At 3 GPa, unit cell dimensions are of about $a = 4.7\text{ \AA}$, $b = 8.1\text{ \AA}$ and $c = 7.8\text{ \AA}$; fractional coordinates are $(1/4, 0.410, 0.179)$ for O and $(1/4, -0.186, 0)$ for C [8]. There are eight water molecules and four methane molecules in the unit cell, implying a water-to-methane molar ratio of 2 to 1. This value is to be compared with the water-to-methane molar ratios of about 6 to 1 encountered in the clathrate phases. During formation of MH-III from methane clathrate hydrate, excess water is expelled. The hydrogen-bonded proton-disordered ice network of MH-III is very close to that of ice Ih and presents six-membered water rings that are

Figure 14. The structure of methane-filled ice Ih (MH-III) in two different crystallographic orientations. The oxygen atoms are shown as red balls and the carbon atoms as black balls. For clarity, the hydrogen atoms have been omitted and the oxygen atoms connected along hydrogen bonds.

aligned to form hexagonal channels along the axis c , as shown in figure 14. Methane molecules are located along the channels at approximately midway between two adjacent six-membered rings, but slightly offset from the centres of the channels in a zigzag arrangement along the c axis. The O atoms of each six-membered ring of MH-III do not bond alternatively to the upper and bottom adjacent rings like in ice Ih but three consecutive O atoms bond to the upper adjacent ring and the remaining atoms bond to the bottom adjacent ring (figure 14). This distortion—compared to ice Ih—creates enough space to accommodate the methane molecules within the structure. It follows that the ice network of MH-III presents two types of alternating channels running along the axis a , namely channels made of large eight-membered water rings which are filled with two non-aligned methane molecules and empty channels made of small four-membered rings.

It is of great interest—both from a fundamental point of view and as the symmetric phase is believed to be the precursor step of a superionic phase [21]—to explore the possibility that the hydrogen bonds connecting the water molecules in structure MH-III symmetrize as pressure is increased. In contrast to ice VII, hydrogen-bond symmetrization in MH-III is complicated by the presence of three different O–O distances. In 2003, a study based on first-principles electronic structure calculations [82] predicted hydrogen-bond symmetrization in MH-III at about 40 GPa. MH-III would then show hydrogen-bond symmetrization at considerably smaller pressures compared to pure ice VII (60 GPa [45,46]) and LiCl- and NaCl-filled ice VII (see previous section). This is somewhat reasonable as O–O distances are shorter in MH-III than in ice VII, and should indeed equal the ‘critical distance’ of 2.42 Å for ice VII at about 40 GPa [7,75], as can be inferred using the experimental lattice parameters reported in [7,75,77] and assuming little change in the atomic coordinates compared to those at 3 GPa. Hirai *et al.* initially suggested that the structural transition they experimentally observed at 40–50 GPa (see above) could have been related to the hydrogen-bond symmetrization [75,76]. However, more recently, the same group investigated both CH₄–H₂O and CH₄–D₂O methane hydrate samples and concluded that the effect of isotopic exchange on the transition is not compatible with hydrogen-bond symmetrization [77]. On the other hand, simulation results by Klug *et al.* [83] suggested that the hydrogen bonds in MH-III should symmetrize only above 60 GPa (i.e. outside the range of stability now accepted for the MH-III structure). Finally, molecular dynamics simulations by Schaack *et al.* [84] confirmed the existence of hydrogen-bond symmetrization in MH-III at about 35–40 GPa in both its frame-hydrogenated and frame-deuterated forms.

Another interesting topic related to the pressure range from 2 to 45 GPa is the expected disorder to order transition for the methane molecules in MH-III. At 2–3 GPa, methane molecules embedded in MH-III are expected to be orientationally disordered [85]. But with increasing pressure, MH-III is supposed to undergo a disorder to order transition for the methane molecules, as also observed in solid methane [86]. Unfortunately, X-ray diffraction is unable to directly establish the ordering of methane.

Figure 15. Pressure dependence of the experimental and computed frequencies of the methane stretching and rocking modes in methane hydrate. Linear fits to the experimental methane stretching frequencies below and above 25 GPa, and to the experimental methane rocking frequencies below 25 GPa are reported as dashed lines.

Hirai *et al.* [76,77] observed a splitting of the methane stretching modes above 15–20 GPa by Raman spectroscopy and a change in the compressibility of the *c* axis by X-ray diffraction at about the same pressure and interpreted both changes as being associated with orientational ordering of the methane molecules in the structure. On the other hand, Klug *et al.* [83] observed a splitting of the antisymmetric CH stretching mode above 19 GPa by infrared spectroscopy and interpreted it as evidence of distortion of the methane molecules and consequent lift of degeneracy of the mode.

To clarify this issue, we performed Raman spectroscopy measurements and ab-initio molecular dynamics simulations of CH₄–D₂O methane hydrate in the MH-III phase at room temperature and pressures up to 45 GPa [14]. For the experiments, the sample was cryo-loaded into a DAC as mentioned above. The density functional theory simulations were carried out by using the Quantum ESPRESSO package [87] in combination with the quantum thermal bath (QTB) implementation [88] or the path integral + generalized Langevin equation (PI + GLE) package [89] to include nuclear quantum effects. The frequencies of the methane stretching and rocking modes obtained from the experimental Raman spectra and from our simulations using the QTB method are reported in figure 15 as a function of pressure. The agreement between experimental and computed frequencies is very good. Our data significantly differ from the previously reported Raman spectra of methane hydrate in the same pressure range [76,77], as we do not observe any splitting of the methane stretching modes above 15–20 GPa. It must be noted however that we measured CH₄–D₂O while previous studies were performed on CH₄–H₂O. The small error bars (smaller than the dots plotted in figure 15) and the large number of pressure points in our measurements allows us to identify a small deviation at approximately 20–25 GPa in the dependence on pressure of the frequencies of both the stretching and rocking modes from a simple linear behaviour. As no structural rearrangements have been observed at this pressure in any of the literature studies [7,75–78] or in our own X-ray diffraction measurement [14], the deviation must correspond to a purely dynamical change. A disorder to order transition for the methane molecules would be the best candidate.

Our extensive analysis of the orientational configuration of the methane molecules from the computed PI + GLE trajectories indeed confirmed this hypothesis [14]. The orientational ordering of the methane molecules with increasing pressure is progressive and passes through several stages. Simulation results indicate that methane molecules rotate almost freely at 2–3 GPa but four favoured orientations are noticeable. Those four methane orientations are represented in figure 16 and noted A₊, A_–, B₊ and B_–. It turned out that rotational motion changing A₊ or A_– into B₊ or B_– is hindered above 5 GPa but motion changing A₊ into A_– and B₊ into B_– is still possible (on the picosecond time scale). Above 20 GPa, all types of rotational motion are

Figure 16. (a) Computed orientational probability density function of the CH bonds of methane in the B_- configuration as a function of the polar angles θ and ϕ at the four indicated pressures. (b) Sketch of structure MH-III with the four methane configurations A_+ , A_- , B_+ and B_- . The oxygen, carbon and hydrogen atoms are shown as red, black and white balls, respectively. Reprinted with permission from Schaack *et al.* [14] (Copyright 2018 American Chemical Society).

hindered. This can be observed in figure 16, which reports the orientational probability density function of the CH bonds of a B_- methane molecule at different pressures computed using the PI + GLE method. Complete locking-in of the rotations is observed at about 20 GPa and this is very likely to explain the change in the slope of the pressure dependence of the vibrational modes in the Raman spectra at about the same pressure (see above). It follows that above 20 GPa methane molecules are arranged in MH-III as $A_+/A_-/A_+$ (or $B_+/B_-/B_+$) along the axis a , as $A_+/B_-/A_+$ (or $A_-/B_+/A_-$) along the axis b , and as $A_+/B_+/A_+$ (or $A_-/B_-/A_-$) along c . On the experimental side, it is also noteworthy that the intensity of the rocking mode of methane strongly increases as pressure is increased from 3 to 20 GPa, likely also as an effect of the progressive orientational ordering of the methane molecules [14].

Finally, we also investigated the changes in the geometry of the methane molecules and the possible mode coupling between methane and water modes upon compression of MH-III. Our simulation results indicate progressive angular distortion of the methane molecules and strong mode coupling between the rocking mode of methane and the stretching modes of water at 30–40 GPa, when their frequencies approach in the experimental spectra, but no evidence of CH bond asymmetry [14]. In summary, our results indicate that, upon compression over the range 2–45 GPa, MH-III evolves from a typical gas-filled ice structure where methane is free to rotate to a mixed molecular crystal where the very distinction between guests and hosts is no more meaningful. It must be emphasized that the orientational ordering of the methane molecules in MH-III is in striking contrast with the almost free rotations observed at ambient pressure in methane clathrate hydrate [90–93] and in comparable systems such as metal–organic frameworks [94].

4. Conclusion

In conclusion, *filled ices*—hosting either ionic or gas species—present marked and somehow complementary differences with respect to the corresponding pure ice phases at the same thermodynamic conditions, though they share similar structures at high pressure.

On the one hand, ions strongly interact with water molecules, act as an internal ‘chemical pressure’ favouring dense phases, and perturb the dipole momentum distribution of water molecules in the ice lattice in such a way that only dense proton-disordered ice phases can hold them in their lattice [16,23]. The presence of ions not only favours water molecules’ orientational disorder but also prevents these high-pressure salty ice phases from being recovered as metastable phases at ambient pressure, such as for high-pressure pure ice phases. Indeed, when pressure is released at low temperature, salty ices transform back to amorphous forms which however differ from the amorphous precursors, i.e. bare memory of their crystallization [18]. For this reason, salty ice crystallization under pressure has been classified as ‘partial’ and the metastable or stable nature of these phases with respect to the separate components remains to be proven. Based on our experimental data, crystalline salty ice phases exist only above 4 GPa. At higher pressures—tens of GPa up to Mbar—the presence of ions prevents the hydrogens to tunnel between the two symmetric positions along the O–O directions in the lattice, thus hindering the transition to the symmetric phase of ice, ice X [17]. This also prevents the protons from delocalizing and thus is likely to give rise to the superionic phase of ice, whose existence in planetary interiors has been proposed [48,49] as a possible explanation for the observed anomalous magnetic moments of planets such as Neptune or Uranus [95]. The ionic conductivity of salty ices is possibly sufficient to give account for the observed magnetic fields.

On the other hand, gases interact weakly with water, and easily fill interstices and channels of low-density ice phases, stabilizing them at much higher pressure than that observed in pure ice phases. Contrarily to salts, the presence of gas molecules reduces the librational/reorientational motions of the bonded water molecules in clathrate structures, which actually obey much stricter geometrical constraints. Furthermore, the presence of gas guests favours proton delocalization in high-pressure hydrate phases and lowers the pressure of the transition to symmetric ice phases [14,84], likely favouring proton diffusion. As is documented in previous studies, while electrical conductivity properties are mostly unchanged, the thermal and vibrational properties of ice clathrates strongly differ from those of crystalline ices, and are rather similar to those of amorphous ice forms [96]. This is likely also the case for high-pressure hydrate phases. In our Raman spectroscopy data on methane hydrate, we have indications of an anomalous flattening of the frequency of the lattice mode as pressure is increased above 30 GPa [14]. The strong coupling between localized guest vibrations and the lattice modes observed in our simulations, could indeed give rise to an unusual pressure and temperature behaviour of the thermal conductivity in this methane-filled ice, as also observed for other mixed molecular solids [97]. However, this point needs to be probed experimentally. Furthermore, the possibility of gas-filled ices transforming to molecular crystals at very high pressure, with markedly different density properties with respect to gas-water mixtures, absolutely needs to be further explored as this is a fundamental point to take into account when modelling the interiors of large icy giants.

Finally, the discovery of anomalous dynamical phenomena such as the observed methane hyper-diffusion at the sI-sII structures interface [13] indicates that the out-of-equilibrium phenomena in these systems are still largely unknown and need to be characterized to provide reliable geodynamical models of icy bodies having ice clathrates as building blocks of their interior.

Data accessibility. This article has no additional data.

Competing interests. We declare we have no competing interests.

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