Ionic ammonia ice

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We report experimental and theoretical evidence that solid molecular ammonia becomes unstable at room temperature and high pressures and transforms into an ionic crystalline form. This material has been characterised in both hydrogenated (NH$_3$) and deuterated (ND$_3$) ammonia samples up to about 180 and 200 GPa, respectively, by infrared absorption, Raman spectroscopy and x-ray diffraction. The presence of a new, strong IR absorption band centered at 2500 cm$^{-1}$ in NH$_3$ (1900 cm$^{-1}$ in ND$_3$) signals the ionization of ammonia molecules into NH$_2^+$ and NH$_3^-$ ions, in line with previous theoretical predictions. We find experimental evidence for a coexistence of two crystalline ionic forms, which our ab initio structure searches predict to be the most stable at the relevant pressures. The ionic crystalline form of ammonia is stable at low temperatures, which contrasts with the behaviour of water in which no equivalent crystalline ionic phase has been found.

I. INTRODUCTION

The properties of ammonia at high pressures and temperatures are important in planetary science and chemistry under extreme conditions. Ammonia has a significant cosmic abundance and it is believed to be a major constituent of the mantles of gas giant planets such as Neptune and Uranus, and numerous extrasolar (exo) planets. The high P-T phase diagrams of ammonia, shown in Fig. 1 and of water have been the subject of recent investigations, leading to the experimental discovery of a “superionic” phase, as previously suggested by ab initio calculations. The latter is characterised by rapid diffusion of protons through the crystalline nitrogen or oxygen lattice and could be relevant for understanding the magnetic fields of giant icy (exo)planets.

The current study concerns the properties of ammonia at high pressures but at lower temperatures than required for stabilising the superionic phase. It has long been thought that solid ammonia would evolve similarly to the isoelectronic water ice with pressure. However, the hydrogen bonds in crystalline ammonia are weaker and more distorted than in water ice, and while the latter evolves continuously towards a symmetric H-bonded solid at around 100 GPa, where protons sit mid-way between two oxygen atoms, no sign of H-bond symmetrisation in ammonia has been found in ab initio calculations up to 300 GPa, or in experiments up to 120 GPa. Nonetheless, recent work has suggested that the molecular ammonia solid is thermodynamically unstable above about 100 GPa at low temperatures, and that it transforms into a crystalline ionic solid phase with a structure of Pma2$\overline{2}$ symmetry consisting of alternate layers of NH$_2^+$ and NH$_3^-$ ions. This ionic solid has not been observed in experiments so far.

We present here a joint experimental and theoretical investigation that provides strong evidences for the existence of an ionic phase of solid ammonia at high pressures. NH$_3$ and ND$_3$ samples have been probed at ambient temperature up to 194 and 184 GPa, respectively,
using Raman scattering, infrared (IR) absorption spectroscopy, and x-ray diffraction techniques. In parallel, \textit{ab initio} theoretical calculations, including new random structure searches, have been carried out in the same pressure range.

II. EXPERIMENTAL AND THEORETICAL METHODS

Liquid NH$_3$ (99.99 \%, Air liquide) and ND$_3$ (99.96 \%, Eurisotop) samples were loaded in membrane diamond anvil cells at 5 bar and 278 K. We used synthetic type IAs diamond anvils (Almax industries) with flat culets of diameter 75 or 50 µm. The gaskets were made of rhenium. The pressure was determined up to 70 GPa from the wavelength shift of ruby fluorescence using the ruby scale from Dewaele \textit{et al.}\textsuperscript{13}, and at higher pressures, from the frequency shift of the first-order Raman band of the diamond anvil tip\textsuperscript{14}.

IR absorption experiments were performed on the SMIS beamline of the SOLEIL synchrotron facility (Saint-Aubin, France) using the FT-IR spectrometer coupled to a vertical microscope. The IR beam was condensed by 15× Cassegrain objectives to a spot of about 25 µm in the focal plane. The sample absorbance is defined as $A = -\log(I/I_0)$, where $I$ is the measured transmitted intensity and $I_0$ the intensity of incident light. To correct for the absorption of the diamond anvils and gasket, we used as $I_0$ the transmission spectra measured in a separate experiment with similar diamond anvils and gasket dimensions but using N$_2$ as sample, which is transparent in the frequency range of interest. Figure 2 shows an example of IR spectra collected from NH$_3$ and N$_2$ at the respective pressures of 40 and 43 GPa, and the calculated absorbance of the NH$_3$ sample.

Raman spectra were collected at each pressure step using a DXR Raman spectrometer from Thermo Fisher with 532 nm exciting laser radiation. Additional Raman spectra were collected with an in-house spectrometer using the 514.5 nm line of an argon laser.

X-ray diffraction experiments were conducted at beamline ID27 of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). We used the angular-dispersive technique with monochromatic x-rays ($\lambda = 0.3738$ Å) and a bidimensional CCD detector (marCCD). The x-ray beam was focussed to a spot of $2 \times 2.6$ µm$^2$ FWHM on the sample. Integration of the x-ray images was performed with the FIT2D software\textsuperscript{15}. Profile refinements were conducted with the FULLPROF software\textsuperscript{16}.

Crystal structure prediction was carried out using the AIRSS method\textsuperscript{17} and the CASTEP code\textsuperscript{18}, with four or eight ammonia formula units, and a target pressure of 125 GPa. Except for the larger number of molecules per unit cell, the same method as in Ref. \textsuperscript{18} was used. For each phase considered, we calculated the enthalpy/pressure/volume equations of state (EOS) up to 400 GPa, using the PWSCF code from the Quantum-Espresso distribution\textsuperscript{19}. These calculations were performed within a standard Density-Functional-Theory framework, using the Perdew-Burke-Ernzerhof gradient corrected functional\textsuperscript{20}, ultrasoft pseudopotential\textsuperscript{21}, and a plane-wave basis set. A kinetic energy cutoff of 50 Ry and k-point grids typically containing 16 to 32 points were used. Other functionals were also tested to check the effect on the molecular-ionic transition pressure, as explained in the next section. The vibrational modes and corresponding Raman and IR spectra were calculated using the PHONON code from the Quantum-Espresso package.

III. RESULTS AND DISCUSSION

Experimental IR and Raman spectra collected on compression of the NH$_3$ samples are shown in Figs. 3 and 4, respectively. Similar graphs for ND$_3$ are reported in Figs. 1 and 2 of the Supplemental Material\textsuperscript{22}. The vibrational spectrum of the molecular NH$_3$-V phase is complex, with 45 Raman and 35 IR non-degenerate active modes\textsuperscript{23}. The strongly absorbing IR bands corresponding to the symmetric bending ($\nu_2 \sim 1450$ cm$^{-1}$ at 137 GPa) and stretching ($\nu_1 - \nu_3 \sim 3000 - 3500$ cm$^{-1}$) vibrational modes saturate the absorption even though the
FIG. 3: (color online) Evolution of the infrared absorption spectra of solid NH$_3$ with pressure. The spectra have been offset for easier visualization. The blue curves are for the molecular phase V, and the red one is for the ionic $\beta$ phase. The frequency window from $\sim$ 2000 to $\sim$ 2300 cm$^{-1}$ is obscured by the strong absorption band of the diamond anvils. Pressures are indicated on the right.

Sample thickness is very small at megabar pressures (5-8 $\mu$m). By contrast, the antisymmetric bending IR bands ($\nu_2$) and Raman active lattice and molecular modes of NH$_3$-V are clearly observed up to 150 GPa. The pressure dependencies of the measured Raman and IR mode frequencies are presented in Figs. 3-5 of the Supplemental Material.

Above 150 GPa, strong changes in the experimental IR and Raman spectra are observed, indicating a transition to another high-pressure phase that we refer to as $\beta$-NH$_3$. The latter is characterised by a new strong and broad IR absorption band around 2300-2800 cm$^{-1}$. The bands in the frequency range corresponding to the bending modes $\nu_2 - \nu_3$ (from $\sim$ 1200 to $\sim$ 1800 cm$^{-1}$) are also very different from those of phase V. The Raman spectrum exhibits a new peak in the antisymmetric stretching frequency range (around 3700 cm$^{-1}$), a large decrease in intensity of the strongest peak of phase V (around 3300 cm$^{-1}$) and the appearance of a broad band around 3000 cm$^{-1}$. Several new lattice Raman peaks also appear at low frequencies, indicating that the new phase has a larger unit cell than phase V (Fig. 4b). Similar changes are observed in ND$_3$ above 150 GPa: the new IR bands in ND$_3$ appear around 1500 cm$^{-1}$ (non saturated) and 1800-2000 cm$^{-1}$ (saturated), a new stretching Raman peak appears at $\sim$ 2750 cm$^{-1}$, and a broad Raman band is observed around 2000 cm$^{-1}$. IR and Raman data were also collected on decompression, the $\beta$ phase was then observed down to 110 GPa before phase V was recovered. The large hysteresis (40 GPa) between the transitions on the upstroke and downstroke suggests a substantial kinetic barrier between the two phases, and therefore a likely change in the molecular bonding at the transition.

The theoretical Raman and IR spectra predicted by...
are consistent with the predicted Raman features of the $\text{Pma2}$ phase. Nevertheless, the newly observed stretching band at about 3700 cm$^{-1}$, as well as the new lattice modes below 300 cm$^{-1}$, are absent in the $\text{Pma2}$ structure, which suggests that this phase alone cannot account fully for the experimental results.

As seen in Fig. 4, there are also some inconsistencies between the measured x-ray diffraction pattern of the $\beta$ phase at 194 GPa and the calculated one for the $\text{Pma2}$ structure. As a matter of fact, although the reflections of the $\text{Pma2}$ structure are present in the experimental pattern, there are several other peaks which it cannot account for. These observations suggest either a larger unit cell, a lower symmetry, or the coexistence of different structures.

New $ab$-$initio$ random structural searches$^{17}$ were therefore undertaken to determine whether other $\text{NH}_3$ structures could exist in the pressure range of our experimental observations. The same method as in Ref. 9 was used, but the maximum number of $\text{NH}_3$ units per unit cell ($Z$) was doubled with respect to the previous work, which used up to 4 molecular units. These searches found the previously reported$^{22}$$\text{Pma2}$ ($Z = 8$) ionic structure and a number of new structures, including an ionic structure of space group $\text{Pca2}_1$ ($Z = 8$). An enthalpy-pressure plot for the most competitive structures is shown in Fig. 7. The $\text{Pma2}$ ionic structure is confirmed to be the most stable between 100 and 176 GPa, while the $\text{Pca2}_1$ ionic structure becomes thermodynamically preferred between 176 and 300 GPa. We have checked whether the appearance of a stable ionic phase is robust to the choice of density functional, finding that each functional tested predicts a transition from the molecular phase $V$ structure ($P2_12_12_1$) to the ionic $\text{Pma2}$ structure. The transition pressure however varies with the functional chosen, ranging from 68 GPa with LDA to 116 GPa with PBE$^{23}$. Table I lists the transition pressures for all cases tested, resulting from previous$^{22,24}$ or the present calculations.

Like $\text{Pma2}$, $\text{Pca2}_1$ is composed of $\text{NH}_4^+$ and $\text{NH}_2^-$ ions, but whereas $\text{Pma2}$ consists of alternate layers of $\text{NH}_4^+$ and $\text{NH}_2^-$ and has a pseudo face-centered cubic (fcc) N-lattice, $\text{Pca2}_1$ is composed of zig-zag chains with a pseudo hexagonal close-packed (hcp) N-lattice (Fig. 6). Another ionic structure of space group $P2_12_12$ ($Z = 8$) was also found, which differs from $\text{Pca2}_1$ only in the orientation of the $\text{NH}_2^-$ ions, but this phase is never stable in the pressure range studied (see Fig. 7). Other, very different structures were found: the “mixed” molecular-ionic $\text{Pmn2}_1$ structure, composed of $\text{NH}_4^+$, $\text{NH}_2^-$ ions and $\text{NH}_3$ molecules, and the $P2_1/m$ structure, composed of $\text{N}^3$ and $\text{NH}_2^-$ ions. Although unstable at 0 K, these structures are close in enthalpy to the $\text{Pma2}$ and $\text{Pca2}_1$ phases, especially the mixed $\text{Pmn2}_1$ structure, which remains within 25 meV/molecule of the $\text{Pma2}$ structure up to $\sim160$ GPa (see Fig. 4). The structural parameters, representations and simulated x-ray patterns of all of the phases discussed above are given respectively in Table 1 and Figs. 6 and 7 of the Supplemental Material$^{24}$.
As shown in Fig. 6, the experimental x-ray pattern at 194 GPa can be interpreted as arising from the coexistence of the fully ionic $Pma2$ and $Pca2_1$ structures: the fitted unit cell parameters are within 1.5% of the theoretical ones (see caption of Fig. 6). This coexistence is reasonable as only a small energy separates the two ionic structures. Since $Pma2$ and $Pca2_1$ phases over a substantial pressure range around 170 GPa.

The x-ray pattern presents too much texture (preferred orientation) to allow the determination of the relative amounts of the two phases from full-profile refinement. Regarding the Raman and IR spectra, the main signature of the ionic species in the $Pca2_1$ structure is, as in $Pma2$, the intense IR modes in the frequency range 2300-2800 cm$^{-1}$, where the molecular phases have no modes at all. In addition, the $Pca2_1$ structure shows strong IR activity around 1900 cm$^{-1}$ and 3700 cm$^{-1}$, and two Raman modes around 3600 cm$^{-1}$, in reasonable agreement with the experimental observations. A coexistence of the two ionic structures therefore matches quantitatively the x-ray data, and qualitatively the Raman and IR data. Clearly, the agreement between the observed and theoretical intensities for the Raman and IR spectra is poor, but as observed above for the molecular $P2_12_1$ phase, this likely originates from the approximations used in the theoretical approach, which is limited to the harmonic level.

We also considered the possibility of a coexistence of the ionic $Pma2$ and mixed $Pmn2_1$ structures. Since $Pmn2_1$ is partially ionic, its Raman and IR spectra have similar features as the $Pma2$ and $Pca2_1$ structures (see Fig. 8 of the Supplemental Material). The Bragg reflections which are not indexed by $Pma2$ or the gasket can also be well indexed by $Pmn2_1$ (see Fig. 9 of the Supplemental Material); however, the ratios of the refined cell parameters for the $Pmn2_1$ structure are $b/a=1.103$ and $c/a=1.248$, which are quite different from the theoretical ones: $b/a=1.046$ and $c/a=1.221$. Since, according to our calculations, the $Pmn2_1$ structure does not have a pressure range of thermodynamic stability, this coexistence model thus appears less likely. The same arguments also militate against coexistence of the molecular $P2_12_1$ phase with $Pma2$ at this pressure. Indeed, the theoretical $b/a$ and $c/a$ ratios for $P2_12_1$ at 200 GPa are 1.736 and 1.631, respectively. These agree well with the extrapolation of experimental data up to 120 GPa, and are largely different from the cell axis ratios which are obtained from our x-ray pattern at 194 GPa. Moreover, the enthalpy difference between $P2_12_1$ and $Pca2_1$ increases rapidly with pressure and exceeds 0.1 eV/molecule at 200 GPa.

Of course, we cannot exclude the possibility that another structure with a larger unit cell – that could result from a more complex stacking of the ionic planes, might explain the experimental data. We emphasise, however, that such a structure must be at least partially ionic to explain the infrared absorption spectrum of the $\beta$-phase. Indeed, whatever the crystallographic structure, the IR band around 2500 cm$^{-1}$ (1900 cm$^{-1}$ in Nd$_3$) in the $\beta$ phase cannot be due to molecular NH$_3$, which therefore implies the presence of NH$_4^+$ ions.
It is interesting to note that all of the crystalline phases of ammonia have a nitrogen sub-lattice that can be described as pure or pseudo-hcp or fcc. This is the case for the proton-disordered molecular phases II (hcp) and III (fcc), and the proton-ordered molecular phases I (pseudo-fcc), IV and V (pseudo-hcp). Even the high P-T superionic α phase may have either a fcc or a pseudo-hcp N lattice, depending on whether it is obtained by compressing phase III or annealing phase V, respectively. Our findings extend this property to the low-temperature ionic phases $Pma2$ (pseudo-fcc) and $Pca2_1$ (pseudo-hcp). Since the N atoms already adopt densely packed configurations and are clearly reluctant to undergo a rearrangement, the “job” of minimising the energy as density increases is accomplished by rearrangements of the H atoms. As pointed out in Ref. [9], the volumes per formula unit of the ionic phases are much smaller than in the molecular ones, because the shapes of the $NH_4^+$ and $NH_2^-$ ions enable them to pack more tightly than $NH_3$ molecules. The ionic structures are therefore favoured at high density. We also note that the $Pca2_1$ structure strongly resembles the $P2_1/m$ ionic phase predicted to be stable above 300 GPa, where $NH_2^-$ ions are linked in zig-zag chains by symmetric H-bonds.

IV. CONCLUSION

In summary, our experimental investigation of solid ammonia to pressures of nearly 200 GPa shows that a transition to a previously unobserved phase, denoted $\beta$, occurs at 150 GPa on compression, which remains stable down to 110 GPa on decompression. The important changes in the Raman and IR active internal modes with respect to the molecular phase V indicate a drastic modification of the intramolecular bonding across the transition. The appearance of intense IR bands in the frequency range around 2500 cm$^{-1}$ makes a strong case in favour of an ionic structure for the $\beta$ phase, composed of $NH_4^+$ and $NH_2^-$ ions, as predicted in a previous theoretical work. The latter has been expanded in the present study, with two main results: first, the predicted transition between the molecular $P2_12_12_1$ and the ionic $Pma2$ around 100 GPa is proved to be robust against the choice of density functional. Second, our new structural searches with up to 8 formula units per unit cell demonstrate that $Pma2$ remains the most competitive phase above 100 GPa at 0 K, and that another ionic structure with space group $Pca2_1$ ($Z = 8$), becomes more stable above 176 GPa. The experimental Raman, IR and x-ray data are best explained by a coexistence of the $Pma2$ and $Pca2_1$ ionic structures near 190 GPa, which is consistent with the small enthalpy difference (\(~\sim\) 15 meV/molecule) between the two phases. Although we cannot presently exclude the possibility that the $\beta$ phase has a different crystallographic structure, with perhaps a larger number of formula units per unit cell, the presence of strong IR absorption in the range of $NH_2^-$ vibrations shows that this structure is composed, at least partially, of ionic species.

Our results confirm that, despite their resemblance at ambient and moderate pressures, $NH_3$ and $H_2O$ follow different structural evolutions at very high densities; while ammonia transforms from a molecular to an ionic ammonium amide solid at megabar pressures, water ice evolves into a symmetric H-bonded solid in the same pressure range. In Ref. [9] it was pointed out that the cost of forming a solid composed of $H_2O^+$ and $OH^-$ units is larger than for solid ammonium amide (1.5 and 0.9 eV/unit respectively). This adds to the fact that water ice can form compact structures accommodating strong and symmetric H-bonds, whereas in ammonia ice the close-packed N-lattice leads to weaker and inequivalent H-bonds that cannot symmetrise without a large deformation of the molecules. We also note that mixtures of ammonia and water have been predicted to form ionic ammonium hydroxide solids under pressure. It would be interesting to extend the present work in this direction, especially since ammonia hydrates are relevant for

### TABLE I: Predicted transition pressures between the molecular $P2_12_12_1$ and ionic $Pma2$ structures according to different DFT functional: PBE, PBE + Tkatchenko-Scheffler van der Waals (TS-vdW) scheme, LDA, HSE06 and PBE0.

| Functional | PBE | PBE+TS-vdW | LDA | HSE06 | PBE0 |
|------------|-----|------------|-----|-------|------|
| P (GPa)    | 97  | 83         | 68  | 126   | 116  |

![Graph showing enthalpy difference (\(\Delta H\)) with respect to the ionic phase $Pma2$ ($Z = 4$) as a function of pressure. The $P2_12_12_1$ structure is isotypic to that reported in Ref. [9]. The other structures were obtained from new structural searches with up to $Z = 8$ formula units per cell.](image)
the description of icy planets and their moons. Finally, further investigations are required to understand the relationship between the static ionic solid found here and the dynamic superionic one reported in Ref. 2 at high P-T conditions.

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1. S. Ninet and F. Datchi, J. Chem. Phys. 128, 154508 (2008).
2. S. Ninet, F. Datchi, and A. M. Saitta, Phys. Rev. Lett. 108, 165702 (2012).
3. J. G. O. Ojwang, R. S. McWilliams, X. Ke, and A. F. Goncharov, J. Chem. Phys. 137, 064507 (2012).
4. M. Bethkenhagen, N. French, and R. Redmer, J. Chem. Phys. 138, 234504 (2013).
5. A. F. Goncharov, N. Goldman, L. E. Fried, J. C. Crowhurst, I. W. Kuo, C. Mundy, and J. M. Zaug, Phys. Rev. Lett. 94, 125508 (2005).
6. J. F. Lin, E. Gregoryanz, V. V. Struzhkin, M. Somoyayzulu, H. K. Mao, and R. J. Hemley, Geophys. Res. Lett. 32, L11306 (2005).
7. C. Cavazzoni, G. L. Chiarotti, S. Scandolo, E. Tosatti, M. Bernasconi, and M. Parrinello, Science 283, 44 (1999).
8. A. D. Fortes, J. P. Brodholt, I. G. Wood, and L. Vodcollo, J. Chem. Phys. 118, 5987 (2003).
9. C. J. Pickard and R. J. Needs, Nat. Mater. 7, 775 (2008).
10. M. Sakashita, H. Yamawaki, H. Fujihisa, and K. Aoki, Rev. High Pressure Sci. Technol. 7, 796 (1998).
11. F. Datchi, S. Ninet, M. Gauthier, A. M. Saitta, B. Canny, and F. Decremps, Phys. Rev. B 73, 174111 (2006).
12. S. Ninet, F. Datchi, S. Klotz, G. Hamel, J. S. Loveday, and R. J. Nelmes, Phys Rev B (R) 79, 100101 (2009).
13. A. Dewaele, P. Loubeyre, and M. Mezouar, Phys. Rev. B 70, 094112 (2004).
14. P. Loubeyre, F. Occelli, and R. LeToullec, Nature 415, 613 (2002).
15. A. Hammersley, S. O. Svensson, M. Hanfland, A. Fitch, and D. Hausermann, High Press. Res. 14, 235 (1996).
16. J. Rodriguez-Carvajal, Physica B 192, 55 (1993), see [http://www.ill.eu/sites/fullprof/].
17. C. J. Pickard and R. J. Needs, J. Phys.: Condens. Matt. 23, 053201 (2011).
18. S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. J. Probert, K. Refson, and M. C. Payne, Z. Kristallogr. 220, 567 (2005).
19. P. Giannozzi and al, J. Phys. Condens. Matter 21, 395502 (2009).
20. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
21. D. Vanderbilt, Phys. Rev. B 41, 7892 (1990).
22. W. L. Mao, H. K. Mao, Y. Meng, P. J. Eng, M. Y. Hu, P. Chow, Y. Q. Cai, J. Shu, and R. J. Hemley, Science 314, 636 (2006).
23. E. Gregoryanz, A. F. Goncharov, R. J. Hemley, and H. K. Mao, Phys. Rev. B 64, 052103 (2001).
24. See Supplemental Material at (URL).
25. S. Ninet, F. Datchi, A. M. Saitta, M. Lazzeri, and B. Canny, Phys. Rev. B 74, 104110 (2006).
26. C. Adamo and V. Barone, J. Chem. Phys. 110, 6158 (1999).
27. G. I. G. Griffiths, R. J. Needs, and C. J. Pickard, Phys. Rev. B 86, 144102 (2012).
28. A. Tkatchenko and M. Scheffler, Phys Rev Lett 102, 073005 (2009).
29. A. V. Krukau, O. A. Vydrov, A. F. Izmaylov, and G. E. Scuseria, J. Chem. Phys. 125, 224106 (2006).
30. M. Gauthier, P. Pruzan, J. C. Chervin, and J. M. Besson, Phys. Rev. B 37, 2102 (1988).