Comparison of the Phase Transitions of High-pressure Phases of Ammonium Fluoride and Ice at Ambient Pressure

Accepted Manuscript: This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination, and proofreading process, which may lead to differences between this version and the Version of Record.

Cite as: J. Chem. Phys. (in press) (2021); <https://doi.org/10.1063/5.0077419>

Submitted: 02 November 2021 • Accepted: 07 December 2021 • Accepted Manuscript Online: 07 December 2021

Zainab Sharif and Christoph G. Salzmann

View Online

Export Citation

CrossMark

ARTICLES YOU MAY BE INTERESTED IN

[Effect of ammonium fluoride doping on the ice III to ice IX phase transition](#)

The Journal of Chemical Physics **154**, 114502 (2021); <https://doi.org/10.1063/5.0032485>

[Detailed crystallographic analysis of the ice V to ice XIII hydrogen-ordering phase transition](#)

The Journal of Chemical Physics **154**, 134504 (2021); <https://doi.org/10.1063/5.0045443>

[Advances in the experimental exploration of water's phase diagram](#)

The Journal of Chemical Physics **150**, 060901 (2019); <https://doi.org/10.1063/1.5085163>

Challenge us.

What are your needs for
periodic signal detection?

Zurich
Instruments

Comparison of the Phase Transitions of High-pressure Phases of Ammonium Fluoride and Ice at Ambient Pressure

*Zainab Sharif and Christoph G. Salzmann**

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, United Kingdom

email: c.salzmann@ucl.ac.uk

9 **ABSTRACT**

10 The phase diagrams of water and ammonium fluoride (NH_4F) display some interesting
11 parallels. Several of the crystalline NH_4F phases have isostructural ice counterparts and one of
12 the famous anomalies of water, the fact that the liquid is denser than ice *Ih*, is also found for
13 NH_4F . Here we investigate the phase transitions of the pressure-quenched high-pressure phases
14 of NH_4F upon heating at ambient pressure with X-ray diffraction and calorimetry, and we
15 compare the results with the corresponding ices. NH_4F II transforms to NH_4F *Isd* which is a
16 stacking-disordered variant of the stable hexagonal NH_4F *Ih* polymorph. Heating NH_4F III
17 gives a complex mixture of NH_4F II and NH_4F *Isd* while some NH_4F III remains initially.
18 Complete conversion to NH_4F *Isd* is achieved above ~ 220 K. The NH_4F II obtained from NH_4F
19 III persists to much higher temperatures compared to the corresponding pressure-quenched
20 NH_4F II. Quantification of the stacking disorder in NH_4F *Isd* reveals a more sluggish conversion
21 to NH_4F *Ih* for NH_4F *Isd* from NH_4F III. In general, the presence of stress and strain in the
22 samples appears to have pronounced effects on the phase transition temperatures. NH_4F shows
23 a complete lack of amorphous forms at low temperatures either upon low-temperature
24 compression of NH_4F *Ih* or heating NH_4F III. The amorphous forms of ice are often used to
25 explain the anomalies of water. It will therefore be interesting to explore if liquid NH_4F displays
26 more water-like anomalies despite the apparent lack of amorphous forms at low temperatures.

27

INTRODUCTION

Kathleen Lonsdale was among the first to realise the structural similarities between the ambient-pressure phases of ammonium fluoride (NH_4F) and ice, both of which showed diffuse star-shaped patterns in their Laue photographs.[1] In fact, the two wurtzite-type materials are difficult to distinguish in X-ray diffraction because of their similar heavy-atom compositions, almost matching lattice constants and shared hexagonal symmetry with NH_4F I and ice *Ih* belonging to space groups $P6_3mc$ and $P6_3/mmc$, respectively.[2, 3] Both NH_4F I and ice *Ih* display decreasing melting temperatures with increasing pressure which means that the liquids of both materials are denser than the corresponding crystalline phases.[4] The famous anomaly of ice floating on water is therefore also found for NH_4F .

Since NH_4F I can contain cubic stacking faults,[5] it has recently been suggested that the stable and fully hexagonal polymorph should be called NH_4F *Ih* in analogy with the nomenclature used for ice.[6] The crystal structure of NH_4F *Ih* is shown in Figure 1. It contains puckered layers consisting of six-membered rings of hydrogen-bonded NH_4^+ and F^- ions in the chair conformation. Upon stacking these layers, additional six-membered rings in the boat conformation form with the heavy-atom positions of a new layer on top of the preceding one. Since only NH_4^+ can hydrogen bond to F^- and vice versa, all ring sizes must be even numbered in NH_4F . This is an important distinction compared to ice where odd-numbered rings of hydrogen-bonded water molecules are possible (see Fig. 3 in ref. [7]). Furthermore, ice can display orientational disorder of the hydrogen-bonded water molecules which gives rise to hydrogen-ordering phase transitions as the molecular orientations become defined at low temperatures.[8] An analogous phenomenon cannot be found for NH_4F .

Figure 1: Crystal structures of (a) $\text{NH}_4\text{F Ih}$, (b) $\text{NH}_4\text{F Isd}$, (c) $\text{NH}_4\text{F II}$, (d) $\text{NH}_4\text{F III}$ and (e) $\text{NH}_4\text{F IV}$. [2, 5, 6, 9, 10] Fluorine, nitrogen and hydrogen atoms are indicated by green, blue and grey spheres, respectively. Covalent N-H bonds are shown as solid grey cylinders and $\text{F}\cdots\text{H}$ hydrogen bonds as dotted lines. For $\text{NH}_4\text{F Ih}$ and Isd , hexagonal and cubic stacking is indicated by 'h' and 'c'. The interpenetrating N-H $\cdots$ F bond in $\text{NH}_4\text{F II}$ is shown as an inset. The fluorine and nitrogen atoms belonging to different hydrogen-bonded networks in $\text{NH}_4\text{F III}$ are indicated in darker and lighter colours. The unit cells are indicated by black lines.

Structural similarities between NH_4F and ice are also found for some of the high-pressure phases. Kuriakose *et al.* showed that the compression of $\text{NH}_4\text{F Ih}$ at ambient temperature to ~ 0.38 GPa leads to the transformation to $\text{NH}_4\text{F II}$. [4] Morosin *et al.* and Wong *et al.* initially assumed $\text{NH}_4\text{F II}$ to be tetragonal. [11, 12] However, further studies showed that a tetragonal cell was insufficient in describing its structure. [5] Other incorrect assumptions were also drawn on the analogy that $\text{NH}_4\text{F II}$ shared aspects of its phase diagram with the other high pressure ammonium halides which led to it being classified as being cubic. [13-15] Lawson *et al.* finally determined $\text{NH}_4\text{F II}$ to be rhombohedral with $R3c$ space group symmetry. [9] In fact, $\text{NH}_4\text{F II}$ is isostructural with ice IV which is a metastable high-pressure phase of ice. [16] The hallmark

feature of the crystal structure of NH_4F II are hydrogen bonds that thread through six-membered rings as shown in Figure 1.

The phase transition from NH_4F *Ih* to NH_4F II and ice *Ih* to ice IV follows a very elegant mechanism first described by Engelhardt and Kamb[17] and now referred to as the Engelhardt-Kamb-collapse (EKC).[6, 9] This mechanism involves the shifting or rotation of layers followed by ‘threading through’ of hydrogen bonds through six-membered rings of the layers above and below to two layers above and below. This pulls all layers closer together resulting in an overall density increase of 37%. It has been argued that this mechanism plays an important role in the formation of high-density amorphous ice (HDA) from ice *Ih* at low temperatures.[6]

Above 1.0 GPa, the cubic NH_4F III (space group $P\bar{4}3m$) forms. It is isostructural with ice VII (space group $Pn\bar{3}m$) and contains two interpenetrating networks that are not hydrogen-bonded to one another as shown in Figure 1.[5] Recently, Bellin *et al.* showed that the compression of NH_4F III beyond 10 GPa yields a tetragonal distortion.[18]

Nabar *et al.* reported X-ray diffraction data recorded upon heating NH_4F II and NH_4F III at ambient pressure from 100 K to room temperature.[5] NH_4F II was found to transform to a new phase, NH_4F V, at ~120 K and to NH_4F *Ih* at ~230 K. Upon heating NH_4F III, two new phases were observed. NH_4F VI formed at ~120 K which then transformed to NH_4F VII at ~200 K. Phases V and VII were attributed to stacking variants of NH_4F *Ih*. The diffraction data in ref. [5] was only reported in terms of the intensity values of the observed reflections and a detailed analysis in terms of the percentages of hexagonal and cubic stacking was not carried out. Regarding NH_4F VI, it was concluded that the powder pattern was too complicated to be analysed unambiguously.

The classification of the metastable NH_4F V and VII forms as stacking-faulted variants of NH_4F I by Nabar *et al.* preceded that of the corresponding ice I polytypes which are now widely recognised as stacking disordered ice (ice *Isd*).[19-22] Ice *Isd* samples are now routinely

analysed for their cubicities (Φ_c) which reflect the percentage of cubic stacking.[20, 23] This is
 achieved by fitting the diffuse diffraction features that arise from the stacking disorder.
 Depending on which high-pressure phase of ice is used as a parent material, ice *Isd* samples
 with different cubicities are obtained upon heating at ambient pressure.[21, 22, 24] For instance,
 ice *Isd* formed by heating ice II yields the highest cubicity of 78 % out of all the high-pressure
 phases.[8] Ices VII and VIII, which are structurally related to NH_4F III, are exceptions with
 respect to the transformations to ice *Isd* upon heating at ambient pressure since they form low-
 density amorphous ice (LDA) before the ice *Isd*. [25-27] Recently, a NH_4F II sample was heated
 to 203 K which gave a stacking-disordered NH_4F sample with a cubicity of 77%. [6] On this
 basis, it was suggested that the label ' NH_4F V' is not needed and that the sample can simply be
 described as NH_4F *Isd* in analogy with the situation for ice.[6] Figure 1 shows a possible NH_4F
Isd structure with a stacking sequence of 'cchchhc' where 'h' and 'c' indicate hexagonal and
 cubic stacking, respectively. In addition to ice I and NH_4F , stacking disorder has recently been
 identified and characterised in a range of structurally related materials including diamond and
 silver iodide.[28, 29] The stacking disorder in these tetrahedrally-bonded materials is somewhat
 more complex than the stacking disorder observed in simple close-packed metals.[30] In
 metals, each stacked layer consists of a flat array of atoms. In the tetrahedrally-bonded materials
 on the other hand the stacked layer units are 'corrugated' bi-layers. This distinction is important
 since the mirror operation associated with hexagonal stacking leads to two symmetry-distinct
 types of layers whereas for metals only one type of layer is needed to describe the stacking-
 disordered structures.

Finally, NH_4F is also known to exist as a plastic phase, NH_4F IV, at temperatures above
 the region of stability of NH_4F II.[10] Its crystal structure is thought to be related to the cubic
 sodium chloride as shown in Figure 1. However, overall, very little is known about this phase
 of NH_4F .

The effect of NH_4F doping on the phase diagram of ice has recently been investigated. It was found that the NH_4F doping selectively removes the hydrogen-ordered ice II from the phase diagram whereas the neighbouring hydrogen-disordered phases readily incorporate the impurity.[31] It was also shown that NH_4F acts as a hydrogen-disordering agent for the hydrogen-ordered ices VIII and IX,[32, 33] and as an inhibitor for the formation of clathrate hydrates.[34, 35]

Most recently, the similarities between ice and NH_4F were explored computationally.[36] It was found that NH_4F departs from ice-like behaviour above ~ 80 GPa where close-packed structures emerge. In analogy to the clathrate hydrates, it was suggested that NH_4F could be a storage material for small guest molecules such as molecular hydrogen.

Here we investigate the phase transitions of NH_4F II and NH_4F III upon heating at ambient pressure from 100 to 270 K using X-ray diffraction and differential scanning calorimetry (DSC). The aims are to clarify the structural nature of the NH_4F VI phase and to test if NH_4F VII can indeed be described as NH_4F *Isd*. The stacking disorder in NH_4F *Isd* will be characterised as a function of temperature by fitting the diffraction patterns with our MCDIFFaX software.[22, 28] The sequence of phase transitions is then compared with those for the structurally related phases of ice. A particularly important point of discussion is the apparent lack of amorphous forms of NH_4F since the isostructural ice displays rich polyamorphism with at least two families of amorphous ices.[37]

MATERIALS AND METHODS

Preparation of NH_4F II and NH_4F III

NH_4F purchased from Sigma Aldrich (catalogue number 216011-100G) with a 98% trace metals basis purity was ground and stored in a desiccator under vacuum. For the preparation of NH_4F II (or NH_4F III), ~ 500 mg (~ 100 mg) of the powder were rapidly transferred into indium cups inside hardened-steel pressure dies and then compressed at 5 kN min^{-1} (1 kN min^{-1}) at

room temperature to 0.6 GPa (1.75 GPa) using a computerised Z100 Zwick Universal Testing Machine. Upon reaching the target pressure, the samples were quenched to 77 K with liquid nitrogen while keeping the pressure constant. After decompression at 77 K, the samples were recovered from the pressure die under liquid nitrogen and freed from the indium for further analysis. The volume changes of a sample recorded upon room-temperature compression to 1.75 GPa are shown in Figure 2. The NH_4F I to NH_4F II phase transition takes place in a narrow pressure range whereas the NH_4F II to NH_4F III transition is more sluggish over a larger pressure range. The respective onset pressures of the phase transitions are 0.418 and 1.317 GPa.

Figure 2: Compression of 102 mg NH_4F Ih at room temperature to 1.75 GPa at 1 kN min^{-1} .

Powder X-ray Diffraction (XRD)

Powders of the recovered NH_4F II and NH_4F III samples were handled under liquid nitrogen and transferred into a purpose-built Kapton-window sample holder for XRD analysis. Diffraction patterns were recorded starting from 95 K using a Stoe Stadi P diffractometer with $\text{Cu K}\alpha 1$ radiation at 40 kV, 30 mA, a monochromating Ge 111 crystal and Mythen 1K linear detector. The cooling of the samples was achieved using an Oxford Instruments CryojetHT. Initial diffraction patterns were recorded at 95 K followed by heating from 100 K to 270 K while collecting diffraction patterns every 10 K for ~20 minutes.

Differential Scanning Calorimetry (DSC)

Small pieces of the high-pressure NH_4F phases were transferred into stainless-steel DSC pans under liquid nitrogen and quickly transferred into a precooled Perkin Elmer 8000 Advanced Double Furnace differential scanning calorimeter. The samples were heated from 93 K at 10 K min^{-1} to room temperature before cooling back to 93 K and reheating. The data recorded during the second heating was subtracted from the first heating run as a background subtraction. After the DSC experiments, the pans were weighed with and without NH_4F to determine the mass of NH_4F . The background subtracted data were then divided by the number of moles of NH_4F and the heating rate to obtain thermograms with units of $\text{J mol}^{-1} \text{K}^{-1}$.

MCDIFFaX analysis

The XRD patterns were fitted using our MCDIFFaX software.[22, 28] The fitted parameters included the lattice parameters, second-order stacking probabilities, peak profile parameters (u , v , w , and Gaussian/Lorentzian ratio) and thermal displacement parameters of N and F. The cubicities were calculated from the second-order stacking probabilities using the equations given in ref. [28].

RESULTS AND DISCUSSION

Figure 3 shows the XRD patterns collected upon heating the NH_4F II sample at ambient pressure. The initial pattern at 95 K is consistent with NH_4F II.[9] Increasing the temperature to 100 K leads to an almost complete loss of NH_4F II and the appearance of broad diffraction features that are characteristic of NH_4F *Isd*. [6] Fitting the pattern with MCDIFFaX gives a cubicity of 76% which changes only slightly upon heating to 200 K where the phase transition to the stable NH_4F *Ih* sets in. This sequence of phase transitions seems approximately consistent with the observations of Nabar *et al.*[5] As mentioned earlier, their NH_4F V is best described as NH_4F *Isd* which may have contained some NH_4F II as can be seen from the positions of the tickmarks shown in Figure 3. Ice IV, the isostructural ice counterpart of NH_4F II, transforms to

185 stacking disordered ice *Isd* at ~ 140 K before the transition to the stable ice *Ih* at ~ 240 K upon
 186 heating at ambient pressure.[38] The cubicity of ice *Isd* made by heating ice IV has not yet been
 187 determined.[38]

188
 189 *Figure 3: Experimental XRD patterns (black lines) and MCDIFFaX fits (red lines) upon heating*
 190 *NH₄F II from 95 K to 270 K at ambient pressure. The tickmarks of NH₄F V are those reported by*

191 *Nabar and co-workers.[5] Asterisks indicate a minor ice Ih impurity that resulted from the sample*
192 *transfer.*

193 Compared to NH_4F II, heating NH_4F III at ambient pressure gives a more complex sequence of
194 phase transitions as shown in Figure 4. The initial pattern at 95 K is consistent with NH_4F III
195 which displays only a small number of Bragg peaks due to its high space group symmetry.
196 Heating to 100 K leads to a phase mixture containing NH_4F II and NH_4F *Isd* as well as some
197 NH_4F III that seems to persist. The Bragg peaks of NH_4F II are considerably broader than those
198 found for the pressure-quenched sample shown in Figure 3 which means that the domain sizes
199 are smaller for the NH_4F II formed by heating NH_4F III at ambient pressure. Upon further
200 heating, the amount of NH_4F II decreases gradually while more NH_4F *Isd* is formed. Yet, small
201 amounts of NH_4F II can still be seen in the patterns up to at least 220 K. This is remarkable
202 considering that the pressure-quenched NH_4F II was lost completely upon heating to 110 K as
203 shown in Figure 3.

Figure 4: XRD patterns (black lines) and MCDIFFaX fits (red lines) upon heating NH_4F III at ambient pressure from 95 K to 270 K. Traces of ice Ih at 95 K are shown by the asterisks. The tickmarks of NH_4F VI and NH_4F VII are those reported by Nabar and co-workers.[5] The tickmarks of NH_4F III were obtained by reduction of symmetry of a corresponding ice VII cell.

MCDIFFaX could only be performed from 200 K onwards, due to the overwhelming presence of additional peaks from other phases.

Because of the $\text{NH}_4\text{F II} / \text{NH}_4\text{F Isd}$ phase mixture, it was not possible to analyse the $\text{NH}_4\text{F Isd}$ diffraction data with MCDIFFaX below 200 K. Heating $\text{NH}_4\text{F Isd}$ from 200 K then leads to a gradual decrease in Φ_c until pure $\text{NH}_4\text{F Ih}$ is found at 260 K.

Nabar *et al.* stated that heating of $\text{NH}_4\text{F III}$ led to the formation of a stacking variant $\text{NH}_4\text{F VI}$ at 120 K which transformed to $\text{NH}_4\text{F VII}$ at 200 K before turning to $\text{NH}_4\text{F Ih}$ at 230 K.[5] On the basis of our data, it can be concluded that their $\text{NH}_4\text{F VI}$ seems to have been a mixture of $\text{NH}_4\text{F II}$ and $\text{NH}_4\text{F Isd}$ which was called $\text{NH}_4\text{F VII}$ once the $\text{NH}_4\text{F II}$ component was lost.[5] Consequently, both $\text{NH}_4\text{F VI}$ and $\text{NH}_4\text{F VII}$ do not seem required to describe the sequence of phase transition observed upon heating $\text{NH}_4\text{F III}$ at ambient pressure.

$\text{NH}_4\text{F III}$ is isostructural with ice VII and its hydrogen-ordered counterpart ice VIII.[8, 32, 39] Heating ices VII and VIII at ambient pressure leads to the formation of LDA at ~110 K, which transforms to ice *Isd* at ~140 K.[27] Using ultra-fast diffraction, Lin *et al.* recently observed that upon heating ice VIII, HDA is transiently observed before the LDA.[40] Notably, amorphous phases are not observed upon heating $\text{NH}_4\text{F III}$. However, judging from the broad Bragg features, both $\text{NH}_4\text{F II}$ and $\text{NH}_4\text{F Isd}$ display quite small domain sizes. The two phases appear in an Ostwald rule-of-stage fashion where $\text{NH}_4\text{F II}$ is more metastable than $\text{NH}_4\text{F Isd}$.

Figure 5 summarises the cubicities of $\text{NH}_4\text{F Isd}$ obtained upon heating $\text{NH}_4\text{F II}$ and $\text{NH}_4\text{F III}$. Interestingly, the changes in Φ_c and therefore the phase transition to $\text{NH}_4\text{F Ih}$ are more abrupt for the $\text{NH}_4\text{F Isd}$ obtained from $\text{NH}_4\text{F II}$. This means that both $\text{NH}_4\text{F II}$ and $\text{NH}_4\text{F Isd}$ from $\text{NH}_4\text{F III}$ display sluggish phase transition kinetics on their way to the stable $\text{NH}_4\text{F Ih}$.

Figure 5: Cubicities of NH_4F Isd upon heating NH_4F II and NH_4F III at ambient pressure up to 270 K. For the NH_4F Isd from NH_4F III MCDIFFaX fits could only be made from 200 K onwards due to the presence of NH_4F II.

The high-pressure phases of NH_4F were also characterised with calorimetry at ambient pressure. Figure 6 shows the DSC traces upon heating (1) NH_4F II and (2) NH_4F III at ambient pressure. In addition to the two pure phases, NH_4F Ih was cold compressed at 77 K to 1.4 GPa as described in ref. [6]. According to XRD analysis, this sample consisted of 70 w% NH_4F II and 30 w% NH_4F Ih. DSC scan (3) in Figure 6 was obtained by heating this sample.

Figure 6: DSC scans of (1) NH_4F II made by compression to 0.6 GPa at room temperature, (2) NH_4F III made by compression to 1.75 GPa at room temperature and (3) NH_4F Ih compressed to 1.4 GPa at 77 K as described in ref. [6] which was found to give 70 w% NH_4F II and 30 w%

NH₄F Ih. All scans were performed at ambient pressure and a heating rate of 10 K min⁻¹. The dashed lines indicate the baselines used for the integrations of the exotherms.

Pressure-quenched NH₄F II transforms to NH₄F *Isd* with an onset temperature of 120 K and the area of the exotherm resulting from the transition was determined as -540.1 ± 6.6 J mol⁻¹. The enthalpy of the corresponding phase transition from the isostructural ice IV to ice *Isd* is -938 ± 14 J mol⁻¹. [38] In analogy to the situation for ice, the phase transition from NH₄F *Isd* to *Ih* appears to be very weak and is not seen in our DSC data.

The thermogram of NH₄F III displays a sharp exotherm with an onset temperature of 116 K and an area of -942.4 ± 63.3 J mol⁻¹ corresponding to the phase transition to a mixture of NH₄F II and NH₄F *Isd*. The baseline after the exotherm is considerably lower compared to before the phase transition which made the integration of the exotherm somewhat difficult. The lower baseline is consistent with a gradual exothermic transformation from NH₄F II to NH₄F *Isd* over an extended temperature range as observed in the XRD analysis in Figure 4. Accordingly, the -942.4 J mol⁻¹ only reflects the heat released during the initial burst of the phase transition and the heat released during the gradual phase transition from NH₄F II to NH₄F *Isd* is not captured in the integration. Increasing the upper integration limit to 240 K gives a heat release of -2010 J mol⁻¹. For comparison, the ice VIII to ice *Isd* phase transition, which includes an intermediate stage of LDA, has an enthalpy change of -2667 ± 25 J mol⁻¹. [41, 42] This means that even with this generous integration limits, the phase transition from ice VIII to ice *Isd* is more exothermic than the corresponding phase transition from NH₄F III to NH₄F *Isd*.

All observed phase transitions of NH₄F were found to be irreversible as demonstrated by cooling NH₄F *Ih* to low temperatures and consistent with NH₄F *Ih* being the thermodynamically stable phase at ambient pressure. In general, the phase transitions of the NH₄F high-pressure phases to NH₄F *Isd* seem to be less exothermic than the corresponding phase transitions of ice. These differences could arise from the underlying thermodynamics of

the two materials. It is interesting to note that NH_4F III forms already at ~ 1.3 GPa upon compression at room temperature (see Figure 2) whereas pressures greater than ~ 2.2 GPa are needed to form ice VII.[8] Hence, smaller differences in free energy would be expected between NH_4F III and NH_4F *Isd* compared to ice VII and ice *Isd* consistent with our calorimetric data. However, this viewpoint does not take into account that ice VII transforms to its ordered counterpart ice VIII upon cooling which leads to a reduction in free energy at low temperatures. Also, since all investigated phase transitions are irreversible, it is difficult to be sure if the heat releases are only governed by the underlying thermodynamics of the bulk phases. For example, irreversible releases of stress and strain in the samples or surface effects in general may also contribute to the observed enthalpies.

The cold-compressed NH_4F *Ih* sample that contains 70 w% NH_4F II and 30 w% NH_4F *Ih* displays an exotherm with an onset temperature of 139 K and an area of $392.3 \pm 33.0 \text{ J mol}^{-1}$. The area of the exotherm seems meaningful since 70% of the 540.1 J mol^{-1} obtained upon heating pure NH_4F II is 378.1 J mol^{-1} which agrees within error with the heat released upon heating the cold-compressed sample. However, the exotherm of the cold-compressed sample is found at a higher temperature and broader compared to the exotherm of the pure and pressure-quenched NH_4F II sample. The higher transition temperature is somewhat surprising. Naively, it could have been assumed that the NH_4F II domains in the cold-compressed sample should experience more strain and stress, and that this reduces its thermal stability. However, evidently, the opposite is the case.

CONCLUSIONS

Heating the high-pressure phases NH_4F II and NH_4F III at ambient pressure has revealed some interesting parallels but also differences compared with the corresponding isostructural ice phases. The pressure-quenched NH_4F II transforms to NH_4F *Isd* upon heating in a similar fashion as the isostructural ice analogue ice IV. For pressure-quenched NH_4F III, a different

behaviour is observed compared to the isostructural ice VII/VIII. Instead of transforming to LDA and later ice *Isd*, heating NH_4F III gives a phase mixture of NH_4F II and NH_4F *Isd* with some NH_4F III persisting initially. This complex phase mixture then transforms gradually to NH_4F *Isd* upon heating. In both cases and consistent with the situation for ice, the stable hexagonal NH_4F *Ih* polymorph is found above 260 K. The previously assigned phase labels NH_4F V, NH_4F VI and NH_4F VII[5] do not seem to be required to describe the sequences of phase transitions observed upon heating NH_4F II and NH_4F III at ambient pressure.

Depending on how NH_4F II is made, it can display very different phase transition properties. The pressure-quenched material, which is highly crystalline according to X-ray diffraction, transforms rapidly at already ~ 100 K. The NH_4F II obtained from NH_4F III at ambient pressure on the other hand displays broad Bragg peaks indicating small domain sizes. Remarkably, small amounts of this NH_4F II persist up to ~ 230 K while it undergoes a gradual phase transition to NH_4F *Isd*. A ‘delayed’ phase transition of NH_4F II to NH_4F *Isd* is also observed for the material cold-compressed at 77 K which also displays broad X-ray diffraction features (see Figure 1 in ref. [6]). For NH_4F , it appears that stress and strain in the material are capable of delaying the phase transitions upon heating. A way to rationalise this is that small domains of NH_4F II are embedded within matrices of more stable NH_4F materials. As the NH_4F II transforms to the lower-density NH_4F *Isd* upon heating, the pressure may rise locally which then counteracts and consequently delays the phase transition.

An interesting parallel between NH_4F and ice is the metastable stage of the stacking disordered material before the phase transition to the stable hexagonal materials at higher temperatures. In light of the recent discovery of fully cubic ice *Ic*, [43-45] a question now arises as to whether a fully cubic NH_4F *Ic* can be prepared. The highest cubicity obtained by us so far is 76%. The preparation of ice *Ic* was achieved through heating of ice XVII.[43] The preparation of the ice XVII relies on removing H_2 from the C_0 clathrate hydrate. The structure of ice XVII

contains five-membered rings. This means that a corresponding NH_4F structure is unlikely and hence this route to $\text{NH}_4\text{F Ic}$ seems difficult. Komatsu *et al.* prepared ice Ic by evacuation of the C_2 hydrogen hydrate.[44] The water network in this clathrate hydrate has the structure of ice Ic with only six-membered rings. A corresponding NH_4F material with H_2 guest molecules could be a promising starting point for making $\text{NH}_4\text{F Ic}$. If $\text{NH}_4\text{F Ic}$ can be prepared, it would be interesting to investigate if it transforms directly to its hexagonal counterpart upon heating as seen for ice[44, 46] or if the conversion takes place *via* stacking disordered intermediates.[45]

Liquid ammonium fluoride certainly deserves further attention. As mentioned earlier, it is anomalous like water in the sense that it is denser than the low-pressure crystalline phase. In the case of water, the existence of two amorphous forms at low temperature and a possible second critical point are often used to explain its anomalies.[47, 48] It will be interesting to investigate if liquid NH_4F displays more water-like anomalies which would be remarkable given the absence of amorphous forms of NH_4F at low temperatures.

ACKNOWLEDGMENTS

Funding is acknowledged from the European Research Council under the European Union's Horizon 2020 research and innovation programme (grant agreement No 725271). We thank M. Vickers and J. Cockcroft for access to the Cryojet, and A. Rosu-Finsen and S. Halukeerthi for help with some of the experiments.

DATA AVAILABILITY STATEMENT

All data were collected in our lab and are available from the corresponding author upon reasonable request.

REFERENCES

- [1] K. Lonsdale, Nature **158**, 582 (1946).

- 342 [2] C. G. V. Beek, J. Overeem, J. R. Ruble, and B. M. Craven, Canadian Journal of
343 Chemistry **74**, 943 (1996).
- 344 [3] B. Morosin, Acta Crystallographica Section B **26**, 1635 (1970).
- 345 [4] A. K. Kuriakose, and E. Whalley, The Journal of Chemical Physics **48**, 2025 (1968).
- 346 [5] M. A. Nabar, L. D. Calvert, and E. Whalley, The Journal of Chemical Physics **51**, 1353
347 (1969).
- 348 [6] J. J. Shephard, S. Ling, G. C. Sosso, A. Michaelides, B. Slater, and C. G. Salzmann, J.
349 Phys. Chem. Lett. **8**, 1645 (2017).
- 350 [7] C. G. Salzmann, P. G. Radaelli, B. Slater, and J. L. Finney, Physical Chemistry
351 Chemical Physics **13**, 18468 (2011).
- 352 [8] C. G. Salzmann, The Journal of Chemical Physics **150**, 060901 (2019).
- 353 [9] A. Lawson, R. Roof, J. Jorgensen, B. Morosin, and J. Schirber, Acta Crystallographica
354 Section B: Structural Science **45**, 212 (1989).
- 355 [10] L. D. Calvert, and E. Whalley, The Journal of Chemical Physics **53**, 2151 (1970).
- 356 [11] B. Morosin, and J. E. Schirber, The Journal of Chemical Physics **42**, 1389 (1965).
- 357 [12] P. T. T. Wong, and E. Whalley, Review of Scientific Instruments **43**, 935 (1972).
- 358 [13] J. Kasahara, I. Ohno, and K. Iida, J. Phys. Earth. **19**, 47 (1971).
- 359 [14] R. Stevenson, The Journal of Chemical Physics **34**, 346 (1961).
- 360 [15] C. A. Swenson, and J. R. Tedeschi, The Journal of Chemical Physics **40**, 1141 (1964).
- 361 [16] H. Engelhardt, and E. Whalley, J. Chem. Phys. **56**, 2678 (1972).
- 362 [17] H. Engelhardt, and B. Kamb, The Journal of Chemical Physics **75**, 5887 (1981).
- 363 [18] C. Bellin, A. Mafety, C. Narayana, P. Giura, G. Rousse, J.-P. Itié, A. Polian, A. M.
364 Saitta, and A. Shukla, Phys. Rev. B **96**, 094110 (2017).
- 365 [19] W. Kuhs, F., D. Bliss, V., and J. Finney, L., J. Phys. Colloques **48**, C1 (1987).

- 366 [20] T. L. Malkin, B. J. Murray, A. V. Brukhno, A. J., and C. G. Salzmann, *Proc. Natl. Acad.*
367 *Sci. USA* **109**, 1041 (2012).
- 368 [21] W. F. Kuhs, C. Sippel, A. Falenty, and T. C. Hansen, *PNAS* **109**, 21259 (2012).
- 369 [22] T. L. Malkin, B. J. Murray, C. G. Salzmann, V. Molinero, S. J. Pickering, and T. F.
370 Whale, *Physical Chemistry Chemical Physics* **17**, 60 (2015).
- 371 [23] T. C. Hansen, M. M. Koza, and W. F. Kuhs, *J. Phys.: Condens. Matter* **20**, 285104
372 (2008).
- 373 [24] H. Y. Playford, T. F. Whale, B. J. Murray, M. G. Tucker, and C. G. Salzmann, *J. Appl.*
374 *Crystal.* **51**, 1211 (2018).
- 375 [25] D. D. Klug, Y. P. Handa, J. S. Tse, and E. Whalley, *J. Chem. Phys.* **90**, 2390 (1989).
- 376 [26] S. Klotz, J. M. Besson, G. Hamel, R. J. Nelmes, J. S. Loveday, and W. G. Marshall,
377 *Nature* **398**, 681 (1999).
- 378 [27] J. J. Shephard, S. Klotz, M. Vickers, and C. G. Salzmann, *J. Chem. Phys.* **144**, 204502
379 (2016).
- 380 [28] C. G. Salzmann, B. J. Murray, and J. J. Shephard, *Diamond and Related Materials* **59**,
381 69 (2015).
- 382 [29] R. L. Smith, M. Vickers, M. Rosillo-Lopez, and C. G. Salzmann, *Crystal Growth &*
383 *Design* **19**, 2131 (2019).
- 384 [30] C. H. Loach, and G. J. Ackland, *Phys. Rev. Lett.* **119**, 205701 (2017).
- 385 [31] J. J. Shephard, B. Slater, P. Harvey, M. Hart, C. L. Bull, S. T. Bramwell, and C. G.
386 Salzmann, *Nat. Phys.* **14**, 569 (2018).
- 387 [32] C. G. Salzmann, Z. Sharif, C. L. Bull, S. T. Bramwell, A. Rosu-Finsen, and N. P.
388 Funnell, *J. Phys. Chem. C* **123**, 16486 (2019).
- 389 [33] Z. Sharif, J. J. Shephard, B. Slater, C. L. Bull, M. Hart, and C. G. Salzmann, *J. Chem.*
390 *Phys.* **154**, doi: 10.1063/5.0032485 (2021).

- 391 [34] K. Shin, I. L. Moudrakovski, M. D. Davari, S. Alavi, C. I. Ratcliffe, and J. A.
392 Ripmeester, *CrystEngComm* **16**, 7209 (2014).
- 393 [35] S. Park, D. Lim, Y. Seo, and H. Lee, *Chem. Comm.* **51**, 8761 (2015).
- 394 [36] L. J. Conway, K. Brown, J. S. Loveday, and A. Hermann, *J. Chem. Phys.* **154**, 204501
395 (2021).
- 396 [37] T. Loerting, K. Winkel, M. Seidl, M. Bauer, C. Mitterdorfer, P. H. Handle, C. G.
397 Salzmann, E. Mayer, J. L. Finney, and D. T. Bowron, *Physical Chemistry Chemical*
398 *Physics* **13**, 8783 (2011).
- 399 [38] C. G. Salzmann, E. Mayer, and A. Hallbrucker, *Physical Chemistry Chemical Physics*
400 **6**, 1269 (2004).
- 401 [39] W. F. Kuhs, J. L. Finney, C. Vettier, and D. V. Bliss, *The Journal of Chemical Physics*
402 **81**, 3612 (1984).
- 403 [40] C. Lin, X. Liu, X. Yong, J. S. Tse, J. S. Smith, N. J. English, B. Wang, M. Li, W. Yang,
404 and H.-K. Mao, *Proceedings of the National Academy of Sciences* **117**, 15437 (2020).
- 405 [41] Y. P. Handa, D. D. Klug, and E. Whalley, *Canadian Journal of Chemistry* **66**, 919
406 (1988).
- 407 [42] S. Klotz, T. Strässle, C. G. Salzmann, J. Philippe, and S. F. Parker, *Europhys. Lett.* **72**,
408 576 (2005).
- 409 [43] L. del Rosso, M. Celli, F. Grazzi, M. Catti, T. C. Hansen, A. D. Fortes, and L. Ulivi,
410 *Nature Materials* 2020).
- 411 [44] K. Komatsu, S. Machida, F. Noritake, T. Hattori, A. Sano-Furukawa, R. Yamane, K.
412 Yamashita, and H. Kagi, *Nature Communications* **11**, 464 (2020).
- 413 [45] C. G. Salzmann, and B. J. Murray, *Nature Materials* **19**, 586 (2020).
- 414 [46] L. Del Rosso, M. Celli, and L. Ulivi, *Nature Communications* **7**, 13394 (2016).
- 415 [47] P. H. Poole, F. Sciortino, U. Essmann, and H. E. Stanley, *Nature* **360**, 324 (1992).

- 416 [48] P. Gallo, K. Amann-Winkel, C. A. Angell, M. A. Anisimov, F. Caupin, C. Chakravarty,
417 E. Lascaris, T. Loerting, A. Z. Panagiotopoulos, J. Russo, J. A. Sellberg, H. E. Stanley,
418 H. Tanaka, C. Vega, L. Xu, and L. G. M. Pettersson, Chem. Rev. **116**, 7463 (2016).

419

(a)

(b)

(c)

(d)

(e)