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Phase Diagram of Ammonium Fluoride to 20 kbar*

A. K. KURIAKOSE† AND E. WHALLEY
Division of Applied Chemistry, National Research Council, Ottawa, Canada

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The phase boundaries and the transition volumes of ammonium fluoride in the range 1 to 20 kbar and 20° to 340°C have been measured, and the transition entropies calculated. A new phase is reported, designated IV, that has an entropy about $R\ln 6$ greater than that of its neighbors I and II. This entropy difference suggests that the ammonium ions in phase IV are orientationally disordered among six equivalent positions. The liquid–I boundary shows that the liquid is mainly ionic.

I. INTRODUCTION

Ammonium fluoride is an interesting substance not only in itself but also because of its close relation to water. Ammonium fluoride I and ice I are isostructural[1] and their lattice parameters and bond distances differ by only about 4%. They appear[2,3] to form a solid solution to the extent of at least several percent ammonium fluoride in ice, although the exact nature of the solution is unknown. No other substance is known to dissolve in ice in more than minute concentrations. NH_3 and HF are isoelectronic with H_2O, and NH_4^+ and F^- are isoelectronic with H_3O^+ and OH^-, respectively. NH_4F, either as $NH_4^+ + F^-$ or as $NH_3 + HF$, is isoprotonic with two water molecules although the protons are distributed differently. Liquid NH_4F should therefore be a model for highly ionized water, and already water ionized to the extent of several percent has been observed[4–6] at 1000°C and 100 kbar. Furthermore, liquid ammonium fluoride has apparently not been made because at atmospheric pressure the solid decomposes before melting, and it is not known whether the liquid is ionic or molecular in structure. A study of ammonium fluoride under pressure should therefore be interesting.

The first study was reported only in 1961 when Stevenson[7] discovered the first high-pressure phase NH_4F II at pressures over 3.8 kbar. Later, Swenson and Tedeschi[8] reported a second-phase NH_4F III that was first observed by Packard and formed at 11.5 kbar at room temperature.

Both Stevenson and Tedeschi and Swenson have speculated on the structures of these phases, Stevenson suggesting that II had the cesium-chloride-like structure adopted by the other ammonium halides, and Tedeschi and Swenson that II had a sodium-chloride-like and III a cesium-chloride-like structure. An x-ray diffraction investigation of II under pressure by Morosin and Schirber[9] showed that the structure of II was much more complicated than either of these suggestions, but the structure could not be determined from the powder patterns.

In the work reported here, the phase diagram has been reinvestigated to 340°C and 20 kbar, a new solid has been found, and the liquid–solid lines have been investigated.

II. EXPERIMENTAL METHODS AND RESULTS

B and A reagent-grade ammonium fluoride was sublimed once in a glass vessel in a stream of dry ammonia gas to inhibit decomposition to ammonium bifluoride and hydrogen fluoride. The voluminous product was removed, except for the part adhering to the glass which was discarded, and was stored in a desiccator. Analysis for water by the Karl Fischer method gave about 0.06%.

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* N.R.C. No. 10061.

† N.R.C. Post-Doctorate Fellow 1965–66. Present address: Norton Co., Chippawa, Ont.

[1] See R. G. W. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1963), 2nd ed., Vol. 1.

[2] R. Brill and S. Zaromb, Nature **173**, 316 (1954).

[3] L. C. Labowitz and E. F. Westrum, J. Phys. Chem. **65**, 408 (1961).

[4] H. G. David and S. D. Hamann, Trans. Faraday Soc. **56**, 1043 (1960).

[5] S. D. Hamann and M. Linton, Trans. Faraday Soc. **62**, 2234 (1966).

[6] W. Holzapfel and E. U. Franck, Ber. Bunsenges. Physik. Chem. **70**, 1105 (1966).

[7] R. Stevenson, J. Chem. Phys. **34**, 346 (1961).

[8] C. A. Swenson and J. R. Tedeschi, J. Chem. Phys. **40**, 1141 (1964).

[9] B. Morosin and J. E. Schirber, J. Chem. Phys. **42**, 1389 (1965).

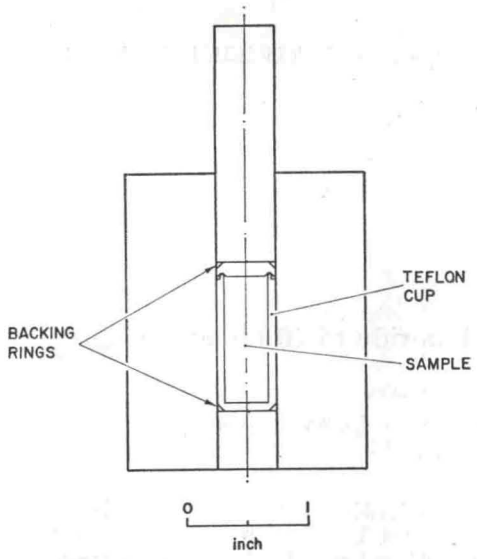


FIG. 1. Section of the pressure vessel. The radial and longitudinal support is not shown.

The high-pressure apparatus was a $\frac{1}{2}$-in. i.d., 2-in. o.d. cylinder of tungsten carbide (2-μm average grain size) in 15% cobalt (Tizit G-30) shown in Fig. 1. At the higher pressures, a steel support ring with 0.018-in. diametral interference provided radial support, and longitudinal support was provided by two steel plates and 15 bolts, as first described by Boyd and England.[10] Pressure was generated by a close-fitting (diametral clearance ~0.0003 in. at zero load) piston driven by a hydraulic press. The cylinder was heated externally by a thermistor-controlled resistance furnace, and the temperature was measured by a Chromel–Alumel thermocouple calibrated against a platinum resistance thermometer and inserted into the lower piston about $\frac{1}{8}$ in. from the sample. The temperature was constant to 0.05°C, and accurate to about 0.1°C.

The ammonium fluoride was usually enclosed in a thin-walled Teflon cup, shown in Fig. 1, with a lip machined to fit a groove in the Teflon cap. A few measurements were done near room temperature without using a cup. Extrusion was prevented by hard-drawn phosphor bronze or hard steel triangular backing rings.

The hydraulic ram was oscillated to reduce friction, and the oil pressure was measured to about 0.3 bar by a

TABLE I. Equilibrium pressures for the transition NH_4F I–II.

Temp. (°C)	Pressure/kbar Up	Down	Temp. (°C)	Pressure/kbar Up	Down
21.5	3.648	3.648	92.9	3.788	...
22.0	3.650	3.650	94.0	...	3.769
23.9	3.696	3.579	95.8	3.823	...
26.8	3.660	...	109.6	...	3.797
31.5	...	3.633	110.8	3.806	...
32.5	3.733	...	114.0	3.823	...
50.8	3.669	...	117.3	...	3.860
54.0	...	3.642	126.8	3.851	...
55.8	3.687	...	128.0	...	3.851
56.1	3.714	...	129.8	3.859	3.850
57.9	...	3.697	131.5	3.878	3.859
62.5	3.715	...	145.9	3.896	...
62.7	...	3.706	147.0	...	3.878
65.5	...	3.696	158.5	3.914	3.896
66.5	3.705	...	159.3	3.896	3.887
73.8	3.760	3.715	159.5	3.896	3.878
75.2	3.773	...	159.8	3.914	...
77.5	...	3.724	160.5	...	3.887
92.5	...	3.760			

[10] F. R. Boyd and J. L. England, J. Geophys. Res. 65, 741 (1960).

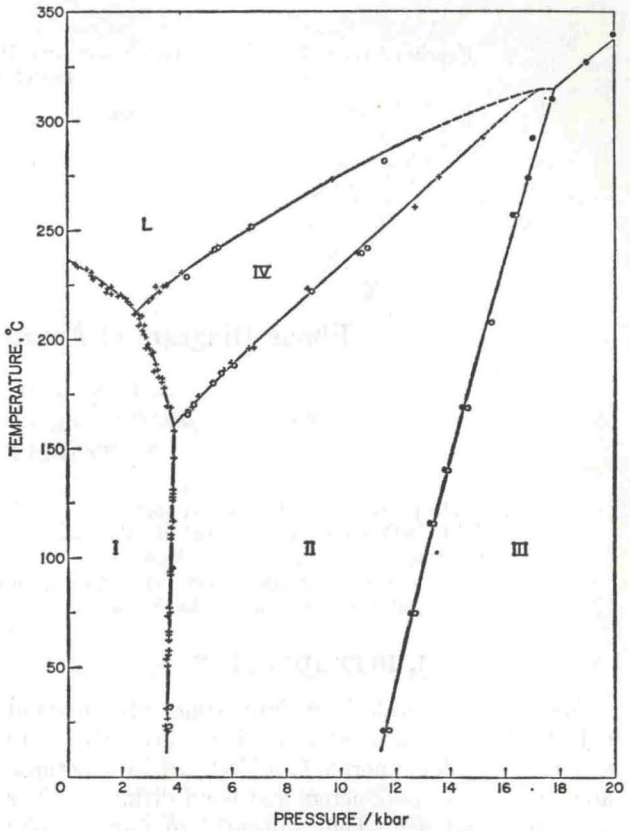


FIG. 2. Phase diagram of ammonium fluoride in the region 0 to 20 kbar, 20° to 340°C. Points marked + had a hysteresis less than 0.1 kbar. Points marked ● and ○ had hysteresis greater than 0.1 kbar and were taken on ascending and descending pressures, respectively.

TABLE II. Equilibrium pressures for the transition NH_4F II–III.

Temp. (°C)	Pressure/kbar Up	Down	Temp. (°C)	Pressure/kbar Up	Down
21.5	11.70	11.52	208.3	15.53	...
75.0	12.70	12.54	257.3	16.42	16.33
116.0	13.39	13.28	274.3	...	16.88
140.5	13.92	13.83	292.5	...	17.06
169.0	14.54	...	310.5	...	17.79
169.5	...	14.48			

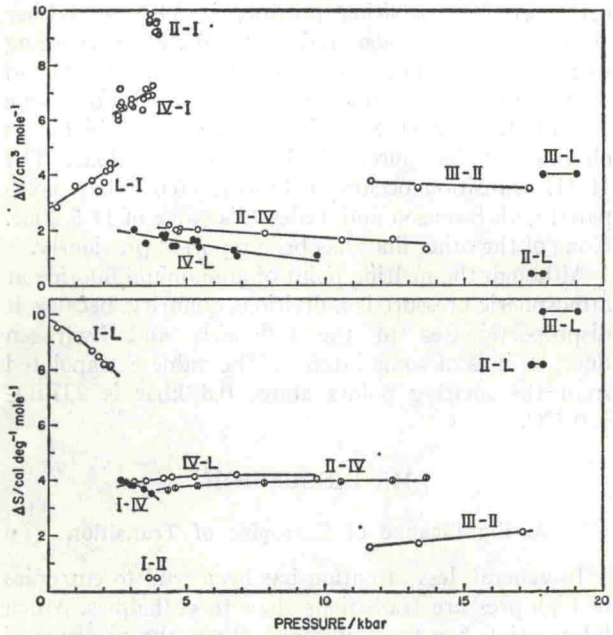


FIG. 3. Volume and entropy changes at the transitions in ammonium fluoride.

TABLE III. Equilibrium pressures for the transition NH_4F I–IV.

Temp. (°C)	Pressure/kbar Up	Down	Temp. (°C)	Pressure/kbar Up	Down
169.3	3.687	3.669	198.1	2.954	...
	3.715				
169.6	3.733	3.733	198.2	2.990	...
178.3	...	3.534	199.0	...	2.970
181.0	3.452	...	200.2	2.918	...
181.3	...	3.452	200.5	...	2.900
181.5	...	3.443	201.1	2.882	...
182.0	...	3.386	201.6	...	2.836
182.9	3.434	3.371	202.5	2.809	...
183.0	3.353	...	202.7	...	2.809
183.3	3.371	3.371	203.5	2.791	...
185.9	3.280	3.262	203.9	...	2.782
185.9	3.217	3.217	206.5	...	2.809
	3.217	3.217			
			209.3	2.628	...
189.1	3.244	3.244			
			210.0	2.620	...
189.4	3.172	3.172			
	3.172	3.172	211.1	...	2.700
193.8	3.801		211.5	2.673	2.628
					2.555
194.8	...	3.081			
			211.9	2.853	2.519
196.3	...	3.008			
			212.1	...	2.555
196.4	3.062	2.908			
			212.3	2.555	...
197.1	2.990	...			
			212.5	2.537	2.564
197.3	...	2.890			
			213.4	2.519	...
197.4	...	2.990			

TABLE IV. Equilibrium pressures for the transition NH_4F II–IV.

Temp. (°C)	Pressure/kbar Up	Down	Temp. (°C)	Pressure/kbar Up	Down
166.8	4.385	...	196.0	...	6.668
167.2	4.440	...	196.1	6.713	...
169.3	...	4.350	196.4	...	6.772
170.6	4.621	...	196.9	6.813	...
174.1	4.829	4.802	222.8	8.892	...
180.1	5.327	...	223.5	...	8.802
180.5	...	5.291	240.0	10.76	10.71
181.0	...	5.345	242.5	10.98	10.87
185.0	5.653	...	261.3	...	12.72
185.6	...	5.726	274.3	...	13.61
188.6	6.097	...	292.5	...	15.24
189.4	...	6.052			

250-bar Heise Bourdon gage, and was monitored by a Statham pressure transducer connected to one axis of an *xy* recorder. The effective area was taken as that of the cylinder corrected for the small elastic distortion. The piston displacement was measured by an Ames dial gage graduated to 10^{-4} in., and was monitored by a Bendix differential transformer acting as a linear displacement transducer, connected to the other axis of the recorder.

Equilibrium pressures were measured by approaching the transition from both lower and higher pressures, and oscillating the piston until the lowest and highest pressure, respectively, was reached. The equilibrium time was usually 5 to 10 min. At 250°C these pressures differed by about 1%, but below 80°C the friction increased, perhaps because of the internal friction of the Teflon, and the difference reached about 3% at room temperature. The results are summarized in Fig. 2 and, where the pressures cannot be read from Fig. 2 to the accuracy of the measurement, are summarized in Tables I–VII. Neither the phase labeled IV nor the liquid have been reported previously.

The liquid phase was shown to be liquid by placing a small monel ball on top of the ammonium fluoride in the Teflon cup. After crossing any of the solid–solid transition lines the ball was always recovered from the

TABLE V. Equilibrium pressures for the transition NH_4F I–L.

Temp. (°C)	Pressure/kbar Up	Down	Temp. (°C)	Pressure/kbar Up	Down
216.3	2.311	...	223.5	1.468	1.495
217.5	2.229	...	224.0	1.609	1.450
219.0	...	2.142	224.0	...	1.486
219.6	1.993	...	225.4	1.269	0.997
220.0	...	2.039	228.0	0.969	...
220.2	...	1.885	228.3	0.978	...
220.4	...	1.994	228.5	0.960	...
220.4	...	1.858	229.6	0.888	...
220.5	...	1.948	232.4	0.707	...
221.5	...	1.631	234.0	0.374	...
221.9	...	1.450	234.8	0.293	...

TABLE VI. Equilibrium pressures for the transition NH_4F IV–L.

Temp. (°C)	Pressure/kbar Up	Down	Temp. (°C)	Pressure/kbar Up	Down
218.0	...	2.963	233.5	4.494	...
219.3	3.098	...	240.7	...	5.291
222.3	3.397	...	241.5	5.400	...
224.3	3.533	3.262	242.5	5.716	...
224.6	3.624	...	251.0	...	6.686
229.3	4.349	4.258	252.3	6.759	...
230.5	...	4.168	273.0	...	9.709
230.8	...	4.186	282.0	11.61	...
230.9	4.195	...	292.5	...	12.88

top, but after crossing a solid–liquid line it was recovered from the bottom.

Volume changes at the transitions were determined, to an accuracy of about 0.2 cm^3 $mole^{-1}$, from the piston displacement as measured by the dial gage and extrapolated to the transition pressure. The known Teflon transitions[11] did not interfere. The results are plotted in Fig. 3. Experimental and smoothed volume changes ΔV and smoothed transition pressures at selected temperatures are summarized in Table VIII.

The pressures and temperatures were plotted on a large-scale graph, and the slopes $(\partial p/\partial T)_e$ of the equilibrium lines were obtained graphically and used in conjunction with the smoothed volume changes in Table VII to determine the entropy changes $\Delta S = \Delta V(\partial p/\partial T)_e$. These are also plotted in Fig. 3 and listed in Table VIII. Near the triple points, the equilibrium lines in Fig. 2 were drawn both to fit the pressures and to make the sum of the volume and the entropy changes at the transitions round the triple point to be zero. The resulting triple points and the properties of the equilibrium curves near the triple points are summarized in Table IX.

The line II–L was not observed directly, although attempts were made to find it, and the line is drawn to be consistent with the known entropy and volume changes II–III and III–L near the assigned L–II–III triple point and II–IV and IV–L near the assigned L–II–IV triple point. The volume change is small and this may explain the failure to find the line. Its existence is not therefore certain. The alternative is that there are III–IV–L and II–III–IV triple points. In addition, the IV–L line near the II–IV–L triple point was not observed, probably because of the small volume change, which can be obtained roughly by extrapolation from lower pressures (see Fig. 2).

The I–II line has been investigated by Stevenson[7] in the temperature range 77° to 300°K and by Swenson and Tedeschi[8] in the range 250° to 400°K, both to a lower accuracy than the present measurements. The agreement is satisfactory. For example, at room temperature, the transition pressure is 3.8±~0.3 kbar according to Stevenson, and 3.8±~0.2 kbar according to Swenson and Tedeschi. Our value of 3.649 obtained without the Teflon cup is almost identical with the value 3.63±0.02 kbar of Morosin and Schirber which was obtained under purely hydrostatic conditions. The II–III transition occurs at 11.61±~0.09 kbar, compared with Swenson and Tedeschi's value of 11.5 kbar. None of the other lines has been reported previously.

Although the melting point of ammonium fluoride at atmospheric pressure is a fictitious quantity, because it disproportionates to the bifluoride and hydrogen fluoride, it is of some interest. The value extrapolated from the melting points above 0.3 kbar is 237.0± ~0.5°C.

III. DISCUSSION

A. Significance of Entropies of Transition

In general, less attention has been paid to entropies of high-pressure transitions than to enthalpies. Much information has been obtained about the presence of orientational disorder from the entropies of transition of molecular crystals,[12] and recently[13] similar information has been obtained about orientational disorder in ionic crystals, particularly the nitrates. In Newns and Staveley's discussion[13], some of the entropies were obtained from the transition volume and the effect of pressure on the transition temperature of atmospheric pressure phases. There have, however, been few discussions[14,15] of the relevance of entropies of transition involving purely high-pressure phases.

The entropy of a crystal can be divided into vibrational entropy S_{vib} and entropy of configurational disorder S_{dis}

$$S = S_{vib} + S_{dis}.$$

We exclude from consideration here crystals in which rotational diffusion contributes to the entropy: however, analogous arguments will hold. The vibrational entropy goes to zero as the temperature goes to zero, and consequently the change of vibrational entropy at a

TABLE VII. Equilibrium pressures for the transition NH_4F III–L.

Temp (°C)	Pressure/kbar Up	Down
327.5	...	19.06
340.0	...	19.96

[11] C. W. F. T. Pistorius, Polymer **5**, 315 (1964) and references quoted there.

[12] See E. F. Westrum and J. P. McCullough, *Physics and Chemistry of the Organic Solid State*, D. Fox, M. M. Labes, and A. Weissberger, Eds. (Interscience Publishers, Inc., New York, 1963), Vol. 1, Chap. 1.

[13] D. M. Newns and L. A. K. Staveley, Chem. Rev. **66**, 267 (1966).

[14] B. Kamb, Acta Cryst. **17**, 1437 (1964).

[15] E. Whalley and D. W. Davidson, J. Chem. Phys. **43**, 2148 (1965).

TABLE VIII. Volume and entropy changes at ammonium fluoride transitions.

Transition	Temp. (°C)	Pressure (kbar)	ΔV/cm³ mole⁻¹ Exptl	ΔV/cm³ mole⁻¹ Smoothed	$(\partial p/\partial T)_e$ (bar deg⁻¹)	ΔS (cal deg⁻¹ mole⁻¹)
I–II	22.5	3.648	−9.88	−9.84	2.0	−0.47
	23.0	3.65	−9.67	−9.80	2.0	−0.46
	129.8	3.85	−9.56	−9.44	2.0	−0.45
	143.0	3.88	−9.60	−9.37	2.0	−0.45
	145.6	3.90	−9.24	−9.32	2.0	−0.45
	158.3	3.91	−9.22	−9.20	2.0	−0.44
II–III	21.5	11.61	−3.83	−3.76	17.8	−1.6
	112.0	13.3	−3.59	−3.68	19.7	−1.7
	292.5	17.3	−3.60	−3.60	24.4	−2.1
I–IV	169.3	3.76	−7.29	−7.12	20.7	3.51
	169.6	3.73	−6.93	−7.10	20.8	3.52
	170.1	3.60	−6.90	−7.04	21.0	3.52
	181.3	3.46	−6.79	−6.99	22.1	3.70
	194.3	3.08	−6.53	−6.76	23.7	3.83
	196.4	3.00	−6.79	−6.68	24.0	3.82
	198.1	2.98	−6.59	−6.67	24.2	3.85
	206.5	2.72	−6.45	−6.48	25.4	3.94
	209.8	2.63	−6.66	−6.45	26.0	3.99
	210.0	2.62	−6.49	−6.44	26.1	4.02
II–IV	166.8	4.34	2.21	2.08	74	3.68
	170.6	4.60	2.04	2.06	77	3.77
	172.0	4.70	2.04	2.04	77	3.74
	181.0	5.40	2.04	2.02	79	3.82
	209.8	7.80	1.94	1.90	86	3.89
	240.0	10.56	1.69	1.79	93	3.98
	261.3	12.40	1.73	1.73	97	4.02
	274.3	13.60	1.42	1.66	104	4.11
I–L	217.2	2.229	−4.45	−4.22	−80.3	8.1
	217.5	2.226	−4.21	−4.21	−81.0	8.1
	219.0	2.07	−4.15	−4.12	−83.0	8.2
	219.6	2.00	−3.74	−4.08	−84.0	8.2
	221.5	1.80	−3.42	−3.96	−89.5	8.5
	224.0	1.56	−3.80	−3.80	−95.5	8.7
	229.6	0.940	−3.60	−3.40	−112.5	9.2
	234.8	0.293	−2.74	−3.06	−130.0	9.5
IV–L	219.3	3.098	2.04	1.88	87	3.91
	224.3	3.54	1.77	1.81	92	3.98
	230.5	4.18	1.87	1.71	100	4.09
	230.8	4.20	1.86	1.70	100	4.09
	233.5	4.48	1.44	1.65	105	4.13
	240.7	5.29	1.64	1.52	114	4.15
	252.5	6.80	1.10	1.26	140	4.22
	273.0	9.68	1.16	0.92	185	4.05

phase change goes to zero. From the Clausius–Clapeyron equation for the equilibrium pressure

$$(\partial p/\partial T)_e = \Delta S/\Delta V,$$

it follows that if two phases that intertransform reversibly have no entropy of disorder, or if each has the same entropy of disorder, then since ΔV is necessarily finite if two phases are to be in equilibrium at 0°K at a fixed pressure, $(\partial p/\partial T)_e$ goes to zero as the temperature goes to zero. Different crystalline phases of the same substance will frequently have similar vibrational spectra, and consequently similar entropy differences at finite temperatures. Then, unless ΔV is small, $(\partial p/\partial T)_e$ will be nearly zero even at finite temperatures. This is the reason why many phase transformations occur at nearly the same pressure over a wide temperature range.

On the other hand, if there is a difference of entropy of disorder at 0°K, then $(\partial p/\partial T)_e$ is finite. If the difference of the entropy of disorder is 1 cal deg⁻¹ mole⁻¹ and the volume change is 1 cm³ mole⁻¹, then $(\partial p/\partial T)_e$ is 42 bar deg⁻¹, which is about a 45° slope on a graph with axes of equal length and representing 20 kbar and 500°C. At finite temperatures, a similar slope will be obtained if the vibrational entropies of the phases are similar and if the volume change is not much smaller than 1 cm³ mole⁻¹. Consequently, order–disorder transformations will frequently have a profound effect on the appearance of high-pressure phase diagrams. Brief discussions of some aspects of these

TABLE IX. Coordinates of the triple points of ammonium fluoride

Triple point	Temp. (°C)	Pressure (kbar)	Boundary lines	ΔV (cm³ mole⁻¹)	ΔS (cal deg⁻¹·mole⁻¹)
I–II–IV	161.0±1.0	3.92±0.04	I–II	−9.3	−0.4
			II–IV	2.1	3.8
			IV–I	7.2	−3.4
I–IV–L	213.0±1.0	2.50±0.04	I–IV	−6.4	4.0
			IV–L	2.0	3.8
			L–I	4.4	−7.8
II–IV–L	314±5	17.4±1.0	IV–II	∼−0.5	∼−4
			II–L	∼0.5	∼8
			L–IV	∼0	∼−4
II–III–L	315±5	17.8±0.4	II–III	−3.6	−2.1
			III–L	∼4.1	∼10.1
			L–II	∼−0.5	∼−8

considerations have been reported in connection with the phase boundaries in ice.[14–16]

B. Transitions I–II and II–III

These considerations can be fruitfully applied to the phase transformations in ammonium fluoride. There is no thermal transition in ammonium fluoride I at zero pressure,[17] and in particular, no order–disorder transformation. If there is orientational disorder in I at 25°C, it is present at 6°K which was the lowest temperature of the thermal measurements. The crystal structure,[1] which is similar to that of wurtzite, appears to be unsuitable for orientational disorder, and it is very likely there is none.

The entropy of the transition I–II is −0.46 cal deg⁻¹·mole⁻¹ at 25°C. This, and the lack of configurational entropy in I requires either that neither phase is orientationally disordered and both have similar vibrational entropies, or that II is disordered but its entropy of disorder is partly compensated by a lower vibrational entropy than I. It seems likely that the first of these possibilities is correct. The reason for this is that if the vibrational entropies of I and II differed by say, 1.5 cal deg⁻¹·mole⁻¹ at 25°C, the difference in vibrational densities of states required would require the entropy difference to change significantly in the experimental range of 25° (−20° if Swenson and Tedeschi's results are included) to 160°C, as it does for the transition II–III (see below). No such change occurs. The similarity of vibrational entropies implies a certain similarity in the densities of the vibrational states in the two phases.

The contraction in the change I→II is about 28% of the zero pressure volume of I. It is surprising that such a large decrease in volume does not stiffen the lattice vibrations more than it appears to. In the transition NH_4F II→III a contraction of 11% is accompanied by a much greater decrease of vibrational entropy (see below).

However, the small entropy change for the I–II transition is not entirely unprecedented. The sum of the entropies of transition at the transformations ice I–III, III–V, V–VI, and VI–VII is only about 0.2 cal deg⁻¹·mole⁻¹, although the sum of the contractions is about 30% of the zero-pressure volume of ice I.[18] The reason for this appears to be that in ice I, III, V, and VI each molecule is hydrogen bonded to four neighbors, with hydrogen bond distances little greater than those in ice I.[16,19–22] The nearest-neighbor bond-stretching and angle-bending potential constants are therefore probably similar in all phases. The lattice dynamics are probably determined mostly by nearest-neighbor potential constants, and so a similar density of states in all phases can be rationalized qualitatively. Ice VII is formed[23] of two interpenetrating ice IC lattices, and each molecule has 8 nearest neighbors, to 4 of which it is hydrogen bonded. Presumably the effect of the increased number of nearest-neighbor interactions is offset by the reduction in the force constants due to the increased hydrogen bond lengths. The structure of ammonium fluoride II is not yet known, and so it is not known whether similar considerations explain the small entropy change I–II.

The entropy change in the transition II–III is −1.6 cal deg⁻¹·mole⁻¹ at 22°C. This is presumably caused by a tightening of the lattice vibrations when III is formed. The loss of entropy becomes greater at higher temperatures, as it should if this were so, and is about −2.1 cal

[16] A. J. Brown and E. Whalley, J. Chem. Phys. **45**, 4360 (1966).
[17] E. Benjamins and E. F. Westrum, J. Am. Chem. Soc. **79**, 287 (1957).
[18] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **47**, 441 (1912); J. Chem. Phys. **5**, 964 (1937).
[19] W. B. Kamb and S. K. Datta, Nature **187**, 140 (1960).
[20] J. E. Bertie and E. Whalley, J. Chem. Phys. **40**, 1646 (1964).
[21] B. Kamb, Science **150**, 205 (1965).
[22] B. Kamb, A. Prakash, and C. Knobler, Acta Cryst. **22**, 706 (1967).
[23] B. Kamb and B. L. Davis, Proc. Natl. Acad. Sci. (U.S.) **52**, 1433 (1964).

$deg^{-1}\cdot mole^{-1}$ at 292°C, which corresponds to a heat capacity C_e along the equilibrium line about 3 cal $deg^{-1}\cdot mole^{-1}$ less for III than for II.

C. Ammonium Fluoride IV

Ammonium fluoride IV is formed from I and from II with a gain in entropy of about 3.6 cal $deg^{-1}\cdot mole^{-1}$, or about $R\ln 6$, where R is the gas constant. By analogy with the I–II transition, the change of vibrational entropy at the I–IV and II–IV transitions is probably small. It is difficult to account therefore for the high entropy change unless there is orientational disorder in IV such that each ammonium ion can occupy any of six different orientations of approximately equal energy. There is at present no direct evidence about the structure of IV, but a little speculation is possible.

Ammonium fluoride I has the 4-coordinated wurtzite structure, and III is closely related to the 8-coordinated cesium chloride structure.[24] The structure of ammonium fluoride II is unknown but x-ray powder diffraction both under pressure[9,24] and on the phase recovered[24] by cooling II to liquid-nitrogen temperature and then removing the pressure, shows clearly that it is not the sodium chloride structure that has been suggested.[8] The sodium chloride phase (I) of the ammonium halides has an entropy of disorder, as obtained from the sum of the entropies of the transitions III–II and II–I quoted by Newns and Staveley,[13] of about $R\ln 6$. This arises because each ammonium ion is 6-coordinated by chloride ions, and it is hydrogen bonded directly to only one of the six.[25,26] Each ion has, therefore, six possible orientations, and occupies them with equal probability. It is possible that ammonium fluoride IV has a similar structure.

D. Liquid Ammonium Fluoride

It is not immediately obvious whether liquid ammonium fluoride is a molecular liquid of NH_3+HF or an ionic liquid. Presumably there are equilibria

$$NH_4^+ + F^- \rightleftharpoons NH_3 + HF,$$

$$HF + F^- \rightleftharpoons HF_2^-, \text{ etc.}$$

If it were a molecular liquid, the density would undoubly be smaller than that of the solid, because the density of liquid ammonia near its freezing point is 0.817 g cm^{-3}, and that of liquid hydrogen fluoride is 0.987 g cm^{-3}, compared with 1.015 g cm^{-3} for ammonium fluoride I. The decrease of volume of 4.2 cm^3 $mole^{-1}$ (at 217°C) on melting I proves that the liquid is essentially ionic.

The liquid promises to be an interesting substance. For example, just as water conducts by an ionization mechanism

$$2\,H_2O \rightleftharpoons H_3O^+ + OH^-,$$

$$H_3O^+ + H_2O \rightarrow H_2O + H_3O^+,$$

liquid ammonium fluoride could conduct by a deionization mechanism as well as by simple ionic migration. For example,

$$NH_4^+ + F^- \rightleftharpoons NH_3 + HF,$$

$$NH_3 + NH_4^+ \rightarrow NH_4^+ + NH_3,$$

$$HF + F^- \rightarrow F^- + HF.$$

The proton transfer step may take place in a single step or via an intermediate F^- ion (for NH_3–NH_4^+ transfers) or NH_4^+ ion (for HF–F^- transfers).

The entropy of melting of NH_4F I extrapolated to atmospheric pressure is 9.8 cal $deg^{-1}\cdot mole^{-1}$ or 4.9 cal deg^{-1} (ion mole)$^{-1}$, compared with 5.26 cal $deg^{-1}\cdot mole^{-1}$ for ice I. The volumes of melting are 1.4 cm^3 (ion mole)$^{-1}$ and 1.62 cm^3 $mole^{-1}$, respectively. The thermodynamics of melting of ice I and ammonium fluoride I are therefore rather similar. The entropy of melting depends on the temperature (or pressure) (see Table VIII) by an amount that corresponds to an increase on melting of the heat capacity along the equilibrium line of about 4 cal $deg^{-1}\cdot mole^{-1}$. The entropy of melting of NH_4F IV is only 3.8 cal $deg^{-1}\cdot mole^{-1}$ at 2.5 kbar; no doubt this is due to the configurational entropy of the orientationally disordered IV.

Ammonium fluoride III has an entropy of melting of about 10 cal $deg^{-1}\cdot mole^{-1}$. The structure of III is not known exactly but it is closely related to the cesium chloride structure.[24] The melting entropies of cesium bromide and iodide, which have the cesium chloride structure at the melting point,[27] are about 6 cal $deg^{-1}\cdot mole^{-1}$. Presumably the difference is largely connected with the vibrational and configurational entropy associated with the rotational motions of the ammonium ion.

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[24] M. A. Nabar, L. D. Calvert, and E. Whalley (to be published).
[25] H. A. Levy and S. W. Peterson, J. Chem. Phys. **21**, 366 (1953).
[26] H. A. Levy and S. W. Peterson, J. Am. Chem. Soc. **75**, 1536 (1953).
[27] See L. Brewer and E. Brackett, Chem. Revs. **61**, 425 (1961).