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Citation: The Journal of Chemical Physics **83**, 5844 (1985); doi: 10.1063/1.449665
View online: http://dx.doi.org/10.1063/1.449665
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/83/11?ver=pdfcov
Published by the AIP Publishing

The nature of ammonium ion disorder in ammonium tetrafluoroaluminate, NH_4AlF_4

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(Received 23 July 1985; accepted 12 August 1985)

In order to clarify previous conflicting reports concerning the existence of an order–disorder phase transition in NH_4AlF_4 at $T \sim 150$ K, the heat capacity of this compound has been measured from $T = 15$ to 305 K, by adiabatic calorimetry. The calorimetric results show a small anomaly in C_p centered at $T = 157$ K ($\Delta S = 0.02$ R), and this is attributed to a soft mode phase transition associated with slight changes in the $(AlF_4)_n^{n-}$ layers. Analysis of the contribution of ammonium ion disorder to the heat capacity indicates that the ammonium ion disorder is gradually thermally excited, and can be adequately described by a three-dimensional Einstein oscillator for which $\theta_E \sim 400$ K. There is no evidence of an order–disorder phase transition association with the ammonium ions.

INTRODUCTION

Because of their high symmetry and relatively weak orientational potentials, ammonium ions in the solid state frequently are found to be disordered at room temperature. The first evidence of such disorder was the calorimetric discovery by Simon in 1922[1] of a phase transition in NH_4Cl at $T = 242.5$ K; this is now known to be the result of the onset of disorder of the ammonium ions between two equivalent orientations in the higher-temperature phase.[2] Indeed, order–disorder phase transitions have been observed in many ammonium salts, and these transitions have been the subject of a large number of experimental and theoretical investigations.[2]

Although most ammonium ions are disordered at room temperature, not all gain their extra degrees of freedom through phase transitions per se. In some cases, the reorientation of the ammonium ions can be considered to be a gradual thermal excitation of a hindered barrier to rotation, leading to disordered ammonium ions at high temperatures, without a change of phase. Examples of ammonium salts of this type include NH_4ClO_4,[3] NH_4ReO_4,[4] and NH_4BF_4.[5]

During the past few years, considerable experimental information concerning ammonium ion disorder has been amassed for another ammonium salt: NH_4AlF_4. Although this salt has been studied by a variety of experimental techniques, the evidence concerning the nature of the disordering process and the existence of polymorphism in this salt was conflicting, as described below.

The general structure of NH_4AlF_4 is that of a layered perovskite, in which corner-sharing AlF_6^{3-} octahedra form the layers and NH_4^+ ions reside in the cavities between the layers. Each ammonium ion is hydrogen bonded to four axial fluorines of the AlF_6^{3-} octahedra, as shown in Fig. 1(a). The AlF_6^{3-} octahedra are slightly rotated with respect to the c-axis, such that adjacent $(AlF_4)_n^{n-}$ layers are rotated in opposite senses [Fig. 1(b)], and the overall room-temperature structure is tetragonal, $I4/mcm$,[6,7] with the NH_4^+ tetrahedra distributed statistically over the two lowest energy orientations shown in Fig. 1(a).

The first evidence concerning polymorphism in NH_4AlF_4 was the report[8] of a phase transition at $T \sim 150$ K from an EPR study of NH_4AlF_4 doped with Fe^{3+}. Neutron diffraction carried out at $T = 5$ and 300 K confirmed the existence of different low- and high-temperature structures; at 300 K the ammonium ions were found to be distributed statistically over the two lowest energy orientations, whereas at 5 K, the ammonium ions were ordered ferrorotationally in the *ab* plane and antiferrorotationally with respect to adjacent planes perpendicular to the c-axis.[7] The AlF_6^{3-} octahedra were found not to be appreciably different at the two

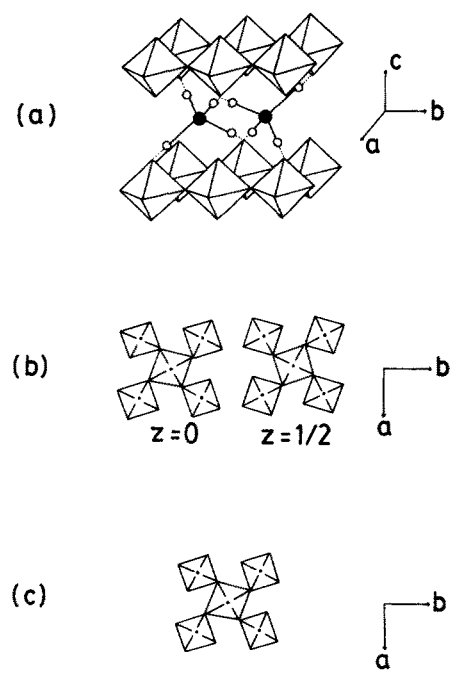

FIG. 1. (a) The structure of NH_4AlF_4, showing the linked AlF_6^{3-} octahedra and the two lowest-energy orientations of ammonium ions. (b) The structure of NH_4AlF_4 showing the different tilts of the AlF_6^{3-} octahedra at two different heights in the unit cell. (c) The structure of $KAlF_4$ showing the tilts of the AlF_6^{3-} octahedra.

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 0021-9606/85/235844-05$02.10

temperatures. Raman spectroscopic studies of NH_4AlF_4 have given additional support for the existence of a three-dimensional order–disorder phase transition resulting almost exclusively from disorder of the ammonium ions[9,10] and more recent EPR experiments of Fe^{3+}:NH_4AlF_4 have been interpreted using a three-dimensional Ising model as a description of the disorder in the ammonium ions.[11]

Although the results of the experiments described above have been interpreted in terms of an order–disorder phase transformation in NH_4AlF_4, other experiments are not consistent with this picture. A nuclear magnetic resonance study of NH_4AlF_4 using ^1H and ^{19}F as probe nuclei, showed[12] that the ammonium ions rotate rapidly and anisotropically at room temperature, and although the spin-lattice relaxation times showed unusual features at the temperature of the reported phase transition ($T \sim 150$ K), both the ^1H and ^{19}F relaxation times were found to be *continuous* throughout that temperature region. This was interpreted as evidence of a second order phase transformation. In addition, a recent infrared spectroscopic investigation, using NH_3D^+ as a probe ion,[13] revealed only gradual changes in the ν_1 and ν_{4bc} absorptions throughout the region of the reported phase transition. Furthermore, a persistent puzzling feature of the supposed phase transformation was the absence of an observable thermal anomaly in a low-temperature differential thermal analysis experiment.[8]

The purpose of the present investigation was to answer the following questions: Is there an order–disorder phase transformation in NH_4AlF_4? What is the nature of the disorder of the ammonium ions in NH_4AlF_4? The experimental technique chosen was the measurement of the heat capacity of NH_4AlF_4 by adiabatic calorimetry.

EXPERIMENTAL

A sample of ammonium tetrafluoraluminate, NH_4AlF_4, was prepared by the thermal decomposition of ammonium hexafluoroaluminate, $(NH_4)_3AlF_6$ (Noah Chemicals), at 250 °C under a stream of dry nitrogen gas.[14] The properties of the product were compared with literature results for Fourier transform infrared spectroscopy[15] and also x-ray powder diffraction;[16] these methods allow an upper limit of 2 mass % for possible starting material or other impurities, notably AlF_3 and NH_4F. The absence of starting material also was confirmed from the calorimetric results which showed no indication of the phase transition of $(NH_4)_3AlF_6$ at $T = 220$ K.[17]

The heat capacity of 11.562 g of NH_4AlF_4 was measured from $T = 15$ to 305 K in an adiabatic calorimeter that was operated in the heat pulse mode. This calorimeter, which consisted of a copper vessel, a single adiabatic shield, and a platinum resistance thermometer, has been described in detail elsewhere.[18] Most of the measurements were taken in the fully automated mode;[19] the experimental precision and accuracy were $\pm$ 1%.

RESULTS AND DISCUSSION

The measured heat capacity of NH_4AlF_4 as a function of temperature is shown in Fig. 2 and given in Table I. (The results were independent of sample history and therefore are given in order of increasing temperature.)

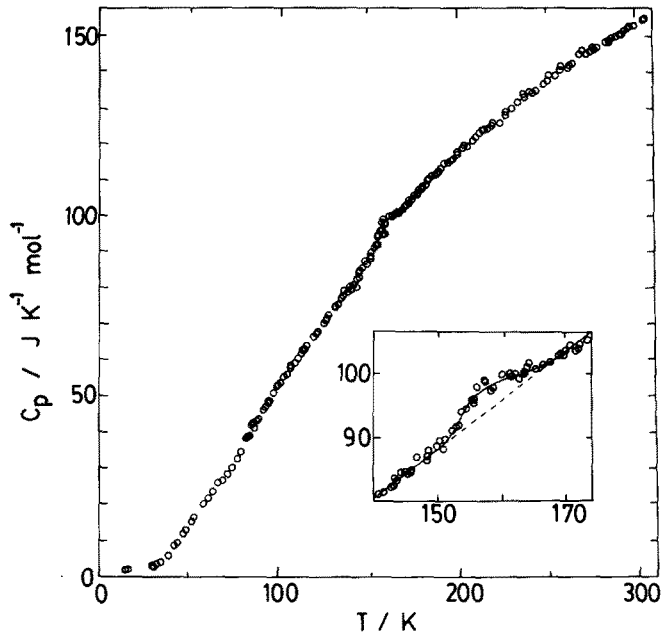

FIG. 2. The experimental values of the heat capacity of NH_4AlF_4 as a function of temperature. The inset is an enlargement of the results around the soft mode phase transition.

It is immediately apparent from Fig. 2 that there is no lambda-shaped singularity in the heat capacity of NH_4AlF_4, as would be expected for an order–disorder phase transformation such as one sees in NH_4Cl,[1] nor is there a very broad shoulder characteristic of the thermal excitation of a hindered barrier to rotation as was observed in NH_4ClO_4,[3] NH_4ReO_4,[4] and NH_4BF_4.[5]

There is, however, an anomaly in the heat capacity of NH_4AlF_4, centered at $T \sim 157$ K, as shown in the inset to Fig. 2. The entropy change associated with this anomaly is very small, about 0.02 R, and the temperature range of the anomaly is about 15 K. There does not appear to be a heat capacity singularity associated with this anomaly. These properties—low entropy change, $\sim$ 15 K temperature range, finite heat capacity—are charcteristic of soft mode phase transitions such as those in malonitrile[20] and *p*-chloranil,[21] and this is likely the source of the heat capacity anomaly in NH_4AlF_4 also.

The existence of a soft mode phase transition at the temperature of the reported phase transition in NH_4AlF_4 fits with the absence of discontinuities in the ^1H and ^{19}F spin-lattice relaxation times in the NMR experiments,[12] and also with the absence of any (observable) thermal anomaly in the differential thermal analysis experiment.[8] In addition, soft mode phase transitions due to rearrangements in the $(AlF_4)_n^{n-}$ layers are well known in other compounds of the general formula $MAlF_4$.[22] Although the Raman experiments on NH_4AlF_4 do not show any evidence of a soft mode in this compound,[9,10] it is quite possible that the associated librational mode is not Raman active; neutron inelastic scattering experiments may elucidate the responsible mode.

The question of disorder of the ammonium ions in NH_4AlF_4 still remains. It is quite certain, especially from the

TABLE I. The experimental values of the heat capacity of NH_4AlF_4.

T (K)	C_p ($J\,K^{-1}\,mol^{-1}$)	T (K)	C_p ($J\,K^{-1}\,mol^{-1}$)	T (K)	C_p ($J\,K^{-1}\,mol^{-1}$)	T (K)	C_p ($J\,K^{-1}\,mol^{-1}$)	T (K)	C_p ($J\,K^{-1}\,mol^{-1}$)	T (K)	C_p ($J\,K^{-1}\,mol^{-1}$)
15.70	1.91	99.56	53.52	139.40	79.95	163.01	99.18	187.77	111.5	240.76	134.4
16.73	1.72	100.53	53.45	140.72	80.90	163.68	100.2	188.84	112.4	240.79	134.7
29.16	3.10	100.56	53.28	141.63	82.19	163.87	100.9	189.91	113.3	244.0	135.1
31.28	2.60	103.08	55.27	142.55	82.14	163.92	99.79	189.95	112.4	244.36	135.6
31.98	3.57	104.93	55.87	143.28	83.74	164.38	101.6	191.45	114.8	246.46	137.5
34.91	4.14	106.25	58.33	143.32	83.22	165.36	100.9	191.61	114.1	247.85	137.1
35.09	4.01	106.66	57.53	143.57	83.26	165.36	100.6	191.79	113.2	247.92	136.7
38.83	5.72	107.15	58.08	144.21	84.67	166.48	101.2	193.75	114.8	251.05	139.5
42.58	8.51	108.88	59.30	145.08	84.60	167.69	101.6	195.18	115.4	251.20	137.8
43.76	9.24	110.42	60.38	145.16	84.24	169.03	102.6	195.32	115.5	255.12	139.4
46.52	11.31	112.46	61.92	145.79	84.31	169.12	103.0	196.89	115.7	258.00	140.6
48.28	12.72	113.12	63.24	145.85	84.71	169.88	102.6	198.43	117.6	258.22	141.9
51.81	15.37	113.82	62.30	145.90	84.77	169.99	103.4	198.44	116.0	261.73	141.5
52.97	16.16	114.77	63.24	146.73	86.82	170.78	104.3	198.61	117.3	262.37	141.9
57.99	19.88	116.00	63.95	148.30	86.94	171.58	103.3	201.52	119.2	264.76	142.7
60.98	21.41	119.13	66.25	148.37	86.12	171.93	103.6	202.49	119.8	268.85	145.1
63.85	23.19	120.30	66.93	148.48	87.89	172.29	104.4	203.82	119.3	269.68	146.1
65.76	25.89	120.47	67.61	149.83	88.58	173.46	105.0	205.12	119.1	271.45	144.9
68.99	26.16	120.74	66.95	150.21	89.38	174.12	105.3	205.40	120.6	272.30	145.6
71.50	27.96	121.62	67.77	150.90	88.01	175.54	104.8	205.59	120.5	276.01	146.8
74.02	29.90	125.47	70.15	151.58	90.58	176.06	106.2	207.90	120.7	276.98	146.2
77.21	34.42	126.63	71.19	152.33	90.90	176.21	106.6	209.78	121.9	278.10	147.1
79.01	34.30	126.73	71.61	152.87	91.58	176.66	107.3	211.83	122.9	279.42	146.8
81.37	38.84	127.02	71.05	153.39	91.68	176.79	105.5	212.42	123.9	283.19	148.2
82.91	38.10	127.78	72.78	153.66	93.99	177.70	107.7	212.60	123.5	284.31	148.6
84.03	39.11	131.83	75.35	154.36	94.34	178.52	107.0	214.28	124.1	284.66	149.2
84.82	41.83	132.17	74.76	155.32	95.76	179.02	108.0	216.72	123.9	286.56	149.5
86.11	42.49	132.18	75.35	155.83	95.88	181.24	108.3	219.46	125.4	290.38	149.9
87.40	40.94	133.00	75.18	156.22	97.81	181.76	109.9	219.65	126.3	291.17	150.8
88.70	43.17	134.61	77.42	157.29	98.99	182.51	109.8	223.66	125.9	281.70	150.7
89.12	43.32	134.83	77.14	157.45	98.73	182.99	109.6	226.52	128.2	293.68	151.5
91.82	46.22	135.48	77.58	148.26	97.14	183.43	110.0	226.70	129.1	297.59	152.7
92.16	46.93	136.55	79.49	158.78	94.59	184.23	111.0	230.57	130.1	297.60	152.6
93.90	48.51	137.35	78.21	158.82	97.74	184.65	110.7	233.63	131.5	299.12	153.0
94.28	47.98	138.10	80.24	160.16	99.73	185.14	110.8	233.74	131.9	303.94	154.9
94.57	48.46	138.35	78.65	161.34	100.0	185.62	110.0	236.68	134.1	304.85	154.9
97.40	50.83	138.91	80.03	161.57	99.50	186.73	111.0	237.49	133.0		

structural studies, that the ammonium ions gain orientational disorder as they are warmed from 5 K to room temperature, and indeed analysis of the ammonium ion contribution to the heat capacity of NH_4AlF_4 supports this conclusion. (*Vide infra.*)

The method usually used to derive the contribution of the ammonium ion to the heat capacity of an ammonium salt is the comparison of the heat capacity of the ammonium compound with that of an isomorphous salt of similar molecular weight and lattice dimensions, such as the corresponding potassium compound.[3–5] The extra heat capacity of the ammonium ion due to its thermally activated disorder, $C(NH_4^+)$, is then given by

$$C(NH_4^+) = C_p(\text{expt.}) - (C_p - C_v) - C_p(\text{K}) - C(NH_4^+,\text{int}), \quad (1)$$

where C_p(expt.) is the experimental heat capacity of the ammonium salt, $(C_p - C_v)$ is the correction from the measured C_p values to C_v values, C_p(K) is the heat capacity of the potassium salt, and $C(NH_4^+,\text{int})$ is the contribution of the internal vibrational modes of the ammonium ion. Equation (1) can be used quantitatively to understand the disorder of the ammonium ions,[3–5] when there is sufficient experimental information available.

In the case of NH_4AlF_4, two factors prevent quantitative use of Eq. (1): the lack of experimental information required to calculate $(C_p - C_v)$ for NH_4AlF_4, and the absence of an isostructural compound to assess the lattice contribution to the heat capacity. The latter problem arises because the corresponding potassium salt, $KAlF_4$, has a structure in which each $(AlF_4)_n^{n-}$ layer has its AlF_6^{3-} octahedra rotated in the same direction with respect to the c-axis,[6] as shown in Fig. 1(c). However, the measured heat capacity for $KAlF_4$[24] can be used semiquantitatively to derive the heat capacity due to disordering of the ammonium ion.

In order to calculate C_v for NH_4AlF_4 from the measured C_p values, one needs to know both the isothermal compressibility and the thermal expansion as a function of temperature. Neither of these appears to have been measured for NH_4AlF_4, and it is not practical to estimate these quantities reliably since the thermal expansion of ammonium salts is sometimes anomalous.[2] However, the correction is usually less than a few percent,[3–5] and therefore we shall ignore this term in Eq. (1). We cannot, however, directly assume that the "lattice" contribution to the heat capacity of NH_4AlF_4 is that of $KAlF_4$, due to their different structures. In fact, the measured heat capacity of $KAlF_4$ exceeds that of NH_4AlF_4 below about 120 K,[23] which indicates that the low frequency

lattice modes are quite sensitive to the subtle structural differences.

In order to calculate the lattice contribution to the heat capacity of NH_4AlF_4, we have employed a method more frequently used in the derivation of low temperature magnetic heat capacities.[24] If we consider the entire lattice to be described by a $3n$-dimensional Debye function, where n is the number of atoms in the molecular formula, one can calculate θ_D, the characteristic Debye temperature, as a function of temperature. If two lattices of similar structure have similar types of thermally excited modes, the θ_D curves for the two compounds will parallel one another as a function of temperature, but if a different type of mode is thermally excited then the curves will deviate from parallel behavior in the temperature region where the "different" mode is substantially activated. Conversely, the temperature dependence of θ_D of one salt can be used to derive the heat capacity of another salt had that different mode not been present, i.e., to calculate the lattice heat capacity, by extrapolating the low-temperature parallel θ_D behavior to higher temperatures. While not as quantitative as Eq. (1), this method has the distinct advantage in cases such as this where no isostructural salt with an atomic cation exists.

Rewriting Eq. (1) using the approximations described above gives the following for the extra heat capacity of the ammonium ion due to its disorder, $C(NH_4^+)$:

$$C(NH_4^+) = C_p(\text{expt.}) - C(\text{lattice}) - C(NH_4^+,\text{int}), \quad (2)$$

where C(lattice) was calculated as described above [observed parallel behavior of $\theta_D(NH_4AlF_4)$ and $\theta_D(KAlF_4)$ for $T < 80$ K extrapolated to higher temperatures] and $C(NH_4^+,\text{int})$ was calculated from the internal vibrational frequencies of an ammonium ion,[25] described as Einstein functions. The disorder heat capacity of the ammonium ion, $C(NH_4^+)$, calculated from Eq. (2), is illustrated as a function of temperature in Fig. 3.

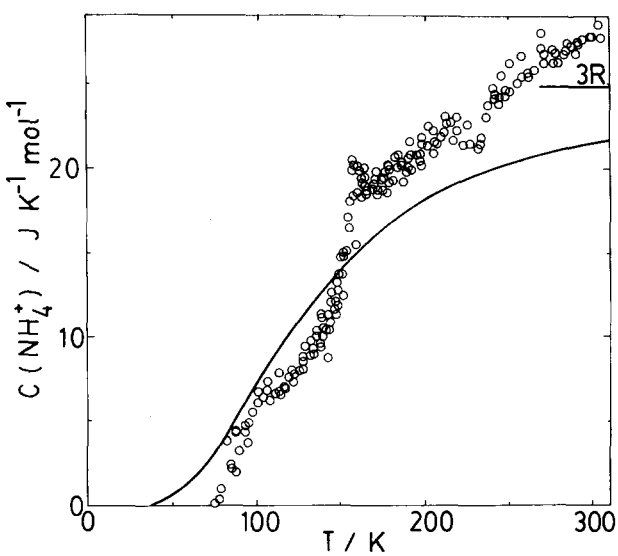

FIG. 3. ○, the heat capacity contribution due to disorder of the ammonium ion in NH_4AlF_4 as a function of temperature, derived as described in the text;—the heat capacity of a three-dimensional Einstein oscillator with $\theta_E \sim 400$ K.

In contrast with ammonium salts in which there is a gradual thermal excitation of a hindered barrier to rotation,[3–5] the disorder contribution to the heat capacity of the ammonium ion in NH_4AlF_4 does not show a characteristic broad maximum as a function of temperature. However, the disorder of the ammonium ion does appear to be thermally excited, climbing to a value slightly in excess of what one might expect for a fully activated vibrational mode 3 R. [The contribution to $C(NH_4^+)$ in excess of 3 R at high temperatures is most likely due to the lack of correction for $(C_p - C_v)$.] This disordering mode can be adequately described as a three-dimensional Einstein oscillator of $\theta_E \sim 400$ K, as given by the solid line in Fig. 3, with a soft mode superimposed at $T \sim 157$ K.

CONCLUSIONS

The heat capacity of NH_4AlF_4 has been determined from $T = 15$ to 305 K in order to answer questions concerning polymorphism in this salt. Previous conflicting reports have been interpreted either in terms of an order–disorder phase transition associated with the ammonium ions, or else have been attributed to gradual transformations from a low-temperature ordered structure to a high-temperature disordered structure. The calorimetric results show no evidence of an order–disorder phase transition in NH_4AlF_4. An analysis of the heat capacity of NH_4AlF_4, in comparison with that of $KAlF_4$, has revealed the gradual thermal excitation of a vibrational mode ($\theta_E \sim 400$ K; $\nu_E \sim 280$ cm^{-1}) that disorders the ammonium ions, in addition to a sort mode at $T \sim 157$ K that is likely due to subtle changes in the AlF_6^{3-} octahedra.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to Professor R. J. C. Brown for his suggestion of these experiments, and also for helpful correspondence and discussions. A discussion with Dr. A. Inaba is also gratefully acknowledged, as are the infrared analyses carried out by Dr. M. Falk and the x-ray powder diffraction experiments done by Mr. G. Owen. This work was supported by the Natural Sciences and Engineering Research Council of Canada.

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