The Crystal Structure of Ammonium Tetrafluoroborate IV at 140°K

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Ammonium tetrafluoroborate shows a transformation from one orthorhombic phase to another at a temperature of 173°K. Both phases have the same space group, *Pbnm*, and the unit cell volume of the low-temperature phase (IV) with cell dimensions of

$$a = 7.243(12)$$
$$b = 8.808(13)$$
$$c = 5.908(22) \text{ Å}$$

is about 1.5% larger than that of the high temperature phase (III). The crystal structure of NH_4BF_4(IV) has been determined at 140°K by standard Weissenberg techniques using visual estimation of intensities and has been refined by full-matrix least-squares methods to a conventional $R = 0.10$. NH_4BF_4(III) and (IV) are very similar and differ mainly in the thermal motion of the BF_4^- and NH_4^+ tetrahedra. In the case of BF_4^- this is apparent only in the slightly different bond parameters observed at low temperature. In the case of NH_4^+, however, localized regions of electron density which can be associated with hydrogen atoms and which are not observable at ambient temperature are observed at 140°K.

Introduction

The alkali metal and ammonium tetrafluoroborates have been found to exist in an orthorhombic phase [1–10] at room temperature and in a cubic phase [11, 12] at high temperatures. In addition, it has been proposed that a different modification of the orthorhombic phase of NH_4BF_4 exists at low temperatures [13, 14]. The crystal structure of the room-temperature orthorhombic phase, NH_4BF_4(III)[1] has been determined by Hoard and Blair [5] and redetermined by Clark and Lynton [16].

In ammonium fluoroborate rotational motion of both the NH_4^+ and BF_4^- ions is to be expected; the presence of reorientational motion in the NH_4BF_4 lattice has been inferred from X-ray work [11], while NMR measurements [12] revealed rapid isotropic tumbling of the BF_4^- ion in the region 472–168°K and the onset of slow isotropic ammonium ion motion between 83 and 20°K.

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[1] The phase designations are taken from ref. (*15*).

According to Pendred and Richards (*17*), the NH_4^+ ion rotates about a C_2 axis at temperatures near 20°K. This is consistent with the NMR data of Chiba (*18*) and of Caron *et al.* (*12*). Stephenson *et al.* (*19*) deduced from thermal data that near 20°K the NH_4^+ ion librates with a barrier of 1.5 kcal/mole. Linewidth transitions for the ^{19}F spin system in the temperature region 133–198°K and for the proton spin system in the region 173–223°K (small) and below 83°K have been observed (*12*).

A low temperature single-crystal X-ray study of NH_4BF_4 was undertaken in order to ascertain the nature and temperature of its low temperature transition and to study the motion of its ions.

Experimental

Crystals were obtained by cold recrystallization of Analar NH_4BF_4. Rectangular prism-shaped crystals of approximate dimensions $0.2 \times 0.2 \times 0.5$ mm³ were sealed into 0.3-mm diameter Lindemann tubes and mounted with the *c*-axis parallel to the instrumental axis on a Weissenberg

camera. Due to cracking upon cooling several crystals were used in the collection of the intensity data.

The crystals were cooled by means of a stream of nitrogen gas, precooled in a copper spiral immersed in liquid nitrogen. The temperature was varied by changing the flow rate and/or the distance of the nitrogen nozzle from the crystal.

Preliminary oscillation photographs taken at 15-degree intervals within the temperature range 300–120°K indicated a phase change in the region 170–185°K. This transition was confirmed by dissimilarities in zero-layer Weissenberg photographs taken at 300 and 200°K and at 165, 140, and 120°K.

Equiinclination Weissenberg photographs (Cu, $K\alpha$, $\lambda = 1.5418$ Å) indicated the space group of the low temperature phase NH_4BF_4(IV) to be the same as that of NH_4BF_4(III) space group $Pbnm$, systematic absences $h0l$; $h + l = 2n + 1$; $0kl$; $k = 2n + 1$. The unit cell dimensions of phase III at room temperature correspond with those published by Clark and Lynton (16); the dimensions for phase IV at 140°K are (estimated SD given in brackets)

$$a = 7.243 \ (.012)$$
$$b = 8.808 \ (.013)$$
$$c = 5.908 \ (.022)$$
$$Z = 4$$

By extrapolation of cell volume (A³) against temperature, it was found that the phase transition III/IV is characterized by a volume increase of ~1.5%. The c-axis especially showed a marked lengthening upon passing to phase IV. The temperature dependences of the crystallographic axes are shown in Fig. 1.

The intensity data for NH_4BF_4(IV) were collected by multiple-film equiinclination Weissenberg photography and were estimated visually by comparison with standard intensity strips. The 163 observed intensities were corrected for Lorentz, polarization and spot size effects; no correction for extinction and absorption was attempted ($\mu R = 0.24$).

All computer programs and scattering factor tables used in this study have been described before (20, 21) and the calculations were performed on an IBM 360/65 computer.

It was assumed that the positions of the nitrogen and boron atoms remained fairly constant during the transition III/IV. Hence a Patterson synthesis was by-passed and a Fourier synthesis
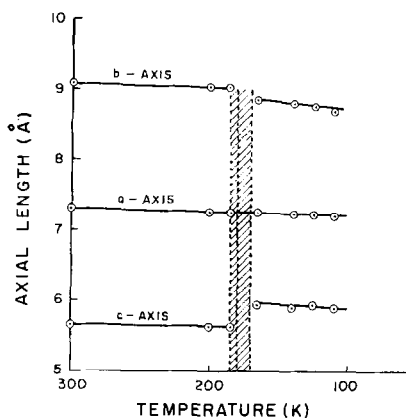

FIG. 1. Temperature dependence of crystallographic axes of NH_4BF_4.

with nitrogen and boron atoms placed in their original phase III positions gave a trial structure that could be refined directly. A full-matrix refinement of the atomic parameters (excluding hydrogen) and isotropic temperature factors was considered complete when all parameter shifts were less than 0.1 of their estimated standard deviations. At this stage the agreement index R was 0.121 for the 163 observed reflections. A difference Fourier synthesis computed at this stage revealed localized areas of electron density (0.8 eA^{-3}) in the vicinity of the nitrogen atom. Interpretation of these maxima as hydrogen atoms reduced the R-factor to 0.100. This decrease is highly significant in terms of Hamilton's test (22), but refinement of the hydrogen positions proved unsuccessful. An attempt to refine the structure in the space group $Pbn2$ was indecisive. The large parameter shifts that were obtained could have been caused by pseudosymmetry and insufficient data and $Pbn2$ is not precluded as a possible space group. Final atomic parameters and standard deviations for phase IV at 140°K, and those of Clark and Lynton (16) for phase III at 300°K, are given in Table I. Table II lists the observed and calculated structure factors. Bond lengths and angles calculated from the final atomic coordinates are listed in Table III. Figure 2 is a stereoscopic pair showing a complete unit cell.

Discussion

An examination of the interatomic distances and angles in the BF_4^- ion indicates little distortion of the BF_4^- tetrahedron at 140°K. Significant,

TABLE I

FRACTIONAL ATOMIC COORDINATES

	$NH_4BF_4(III)^a$			$NH_4BF_4(IV)$ at 140°K			
Atom	x	y	z	x	y	z	Isotropic B
B	0.6920	0.0605	0.2500	0.6905	0.0722	0.2500	1.223
$F_{(1)}$	0.6101	0.9234	0.2500	0.5822	0.9403	0.2500	2.406
$F_{(2)}$	0.5642	0.1728	0.2500	0.5764	0.2019	0.2500	1.571
$F_{(3)}$	0.8039	0.0755	0.0499	0.8060	0.0768	0.0527	1.469
N	0.1642	0.1853	0.2500	0.1714	0.1843	0.2500	0.704
$H_{(1)}$	—	—	—	0.1300	0.2900	0.2500	3.000
$H_{(2)}$	—	—	—	0.2700	0.1900	0.2500	3.000
$H_{(3)}$	—	—	—	0.1000	0.1500	0.0800	3.000

[a] Room temperature data by Clark and Lynton (16).

however, is the lengthening of the B–F bonds upon undergoing the phase transition. This lengthening correlates with the linewidth transition observed for the BF_4^- ion in the region 198–133°K. The positions of the F–atoms in phase III are clearly affected by severe thermal motion, but below 173°K[2] libration of the BF_4^- tetrahedra is minimal as evidenced by the observed Debye–Waller factors.

The ammonium ion was found to be less symmetric than the anion; observed N–H distances ranged from 1.17 to 0.867 Å and the tetrahedral H–N–H angles from 118–96.3°. As the hydrogen positions could not be refined too much significance should not be attached to the relative nonideality indicated by these values. What is significant is that definite regions of electron density were found and interpretation of these as hydrogen atoms gave satisfactory results.

A seemingly paradoxical situation now exists, as localized hydrogen positions are in direct opposition to single crystal NMR and heat capacity results which support freely rotating ammonium ions at this temperature. It is, however, well established that a phase transition III/IV occurs at 173°K whereby the BF_4^- ions became completely ordered and the motion of the ammonium ion is changed. Seen from an X-ray point of view the motion of the ammonium ion changed from a completely disordered distri-

[2] Temperature of the phase transition III/IV as found by infrared work by Schutte and van Rensburg—ref. (23).

bution of hydrogen atoms about the central nitrogen atom (in phase III) to a motion wherein the hydrogen atoms are localized at the expected bonding distances in discrete regions around the nitrogen atom. These regions correlate reasonably well with expected hydrogen positions for a tetrahedral NH_4^+ ion. Low-temperature infrared studies (23) also indicate a change in rotational motion below 173°K—the formation of one (or more) weak hydrogen bonds was invoked (23) to explain this effect. In $H_3N \cdot BF_4$ (24) and $H_2N \cdot BF_3$ (25) where weak hydrogen bonding is suggested the N–H–F distances are 3.03 Å, whereas strong hydrogen bonded systems give N–H–F distances of 2.6–2.8 Å (26, 27). An examination of all the N–F distances in $NH_4BF_4(IV)$ at 140°K show that they are too long for strong or medium hydrogen bonds. There is, however, the possibility of weak hydrogen bonds existing below 173°K—the N–F$_1$ distance of 2.90 Å and N–H$_1$–F$_1$ angles of 149° and/or N–F$_2$ distance of 2.94 Å and N–H$_2$–F$_2$ angle of 171.4°K represent two distinct possibilities. See Table IV for the relevant data.

One of the surprising features of the phase transition is the volume increase. A similar volume increase on transition to a low temperature polymorph has been observed for the cubic–tetragonal transition of NH_4Br and NH_4I (28). The tetragonal phase contains columns of NH_4^+ ions ordered in two types of orientation along the c-axis and in the high temperature phase these two orientations occur at random. The ordered phase is stabilized by electrostatic

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS ($\times10$) OF AMMONIUM FLUOROBORATE IV

h	k	F_o	F_c
L=0			
2	0	406	-371
4	0.	154	-156
8	0	291	288
1	1	129	-135
2	1	200	-220
3	1	381	-381
4	1	156	-158
5	1	374	368
0	2	209	199
1	2	362	372
2	2	225	-234
3	2	236	-238
4	2	77	70
7	2	131	106
2	3	547	595
3	3	122	122
4	3	75	-82
6	3	142	159
7	3	75	-62
8	3	87	-78
0	4	117	-118
1	4	473	432
2	4	192	175
3	4	-104	-106
5	4	246	-246
6	4	98	-81
7	4	217	241
1	5	161	-152
2	5	297	290
3	5	88	54
4	5	56	-72
6	5	87	73
7	5	127	114
0	6	317	-319
1	6	51	54
2	6	184	186
1	7	121	106
2	7	93	-110
3	7	129	158
4	7	88	91
5	7	245	-206
0	8	449	-428
1	8	173	-192
2	8	87	102
4	9	50	80
1	10	73	-95
3	10	61	96
L=1			
1	0	338	367
3	0	340	351
5	0	202	213
2	1	384	-325
3	1	236	209
4	1	192	-189
5	1	118	-128
7	1	98	-71
0	2	422	-427
1	2	336	327
2	2	243	251
3	2	101	-97
5	2	116	-101
6	2	117	-113
7	2	80	82
8	2	107	101
1	3	370	-320
2	3	216	191
5	3	150	132
7	3	119	111
0	4	361	362
2	4	274	265
3	4	81	99
4	4	154	-157
6	4	145	-142
1	5	125	-103
2	5	180	-196
5	5	69	77
7	5	34	47
0	6	133	-151
1	6	211	-241
5	6	57	54
2	7	134	150
4	7	80	113
0	8	80	125
1	8	57	-88
3	8	69	-93
5	8	57	-82
1	10	46	-22
2	10	43	-98
L=2			
2	0	354	-362
4	0	189	207
6	0	175	158
8	0	37	54
1	1	388	416
2	1	370	380
3	1	212	-248
4	1	133	-148
5	1	57	86
6	1	88	115
7	1	193	-171
0	2	337	336
1	2	330	348
2	2	174	-154
3	2	81	-106
5	2	41	-74
6	2	44	59
7	2	76	84
8	2	49	-72
4	3	441	-432
5	3	112	115
6	3	148	140
0	4	211	-174
1	4	244	246
3	4	237	209
5	4	169	152
8	4	38	32
3	5	286	260
4	5	182	-190
5	5	244	-222
6	5	75	86
0	6	166	-184
1	6	56	63
2	6	180	163
6	6	136	-91
7	6	40	32
1	7	237	-214
3	7	134	136
0	8	126	145
2	8	63	75
3	8	116	85
4	8	56	-73
5	8	33	28
2	9	201	-168
4	9	132	113
0	10	101	-36
L=3			
1	0	192	192
3	0	422	-442
5	0	193	-207
7	0	187	153
1	1	137	-125
2	1	431	439
4	1	195	-154
6	1	203	160
7	1	121	107
0	2	172	-141
1	2	75	48
2	2	110	87
1	3	61	69
2	3	87	-91
3	3	319	306
5	3	359	-324
0	4	503	-572
1	4	115	-100
4	4	71	78
3	5	201	178
4	5	195	156
5	5	208	-188
3	6	52	73
2	7	257	-250
3	7	90	-96
4	7	50	71
2	8	72	-83
3	8	143	128
2	9	73	-79
4	9	27	64

TABLE III

INTERATOMIC DISTANCES AND ANGLES FOR NH_4BF_4(III) (16) AND IV WITH ESTIMATED STANDARD DEVIATIONS IN BRACKETS

Interatomic distance	NH_4BF_4(III) distance in Å	NH_4BF_4(IV) distance in Å
$B-F_{(1)}$	1.379(07)	1.411(18)
$B-F_{(2)}$	1.379(07)	1.410(20)
$B-F_{(3)}$	1.404(04)	1.434(16)
$F_{(1)}-F_{(2)}$	2.286(06)	2.309(12)
$F_{(2)}-F_{(3)}$	2.261(04)	2.305(12)
$F_{(3)}-F_{(3)}$	2.272(03)	2.322(20)
$F_{(1)}-F_{(3)}$	2.277(05)	2.330(13)
$N-H_{(1)}$	—	0.976(-)
$N-H_{(2)}$	—	0.867(-)
$N-H_{(3)}$	—	1.171(-)
$H_{(1)}-H_{(2)}$	—	1.404(-)
$H_{(2)}-H_{(3)}$	—	1.759(-)
$H_{(3)}-H_{(3)}$	—	2.008(-)
$H_{(1)}-H_{(3)}$	—	1.605(-)
N-B	3.618(07)	3.622(23)
N-B	3.663(05)	3.653(16)
N-B	3.729(05)	3.850(16)
N-B	—	3.880(23)

Bonds	NH_4BF_4(III) angle in degrees	NH_4BF_4(IV) angle in degrees
$F_{(1)}-B-F_{(2)}$	111.98(37)	109.97(1.4)
$F_{(1)}-B-F_{(3)}$	109.79(36)	110.69(1.4)
$F_{(2)}-B-F_{(3)}$	108.60(34)	108.45(1.0)
$F_{(3)}-B-F_{(3)}$	107.99(33)	108.53(1.2)
$H_{(1)}-N-H_{(2)}$	—	99.11(-)
$H_{(1)}-N-H_{(3)}$	—	96.36(-)
$H_{(2)}-N-H_{(3)}$	—	118.61(-)
$H_{(3)}-N-H_{(3)}$	—	118.04(-)

interaction between neighbouring NH_4^+ ions and should any random reorientations occur this interaction will cause a return to the ordered structure. Increase in temperature however, increases the rate of random reorientation and eventually destroys the coherency of the electrostatic interactions and leads to an order–disorder transition which for the ammonium halides occurs at a temperature of about 100°K above the linewidth transitions.

In NH_4BF_4 the NH_4^+ linewidth transition was observed (12) at about 80°K while the III–IV transition occurs at 173°K to suggest a transition
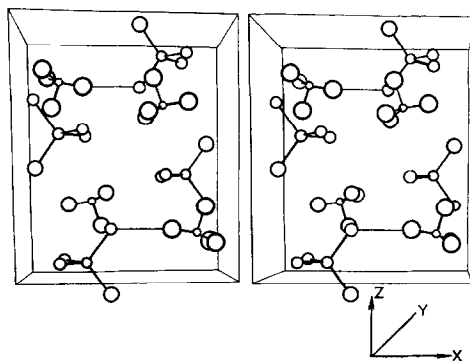

FIG. 2. Stereoscopic drawing of the complete NH_4BF_4-(IV) unit cell. The larger spheres represent hydrogen atoms.

TABLE IV

CLOSEST N–F DISTANCES AND ANGLES

Atoms	NH₄BF₄(III) distance (Å) (16)	NH₄BF₄)IV) distance (Å)
N–F₁	2.942(07)	2.900(17)
N–F₃	2.926(04)	2.925(15)
N–F₃	2.939(04)	2.927(14)
N–F₂	2.914(05)	2.935(17)
N–F₃	2.942(07)	3.044(14)
N–F₂	3.026(05)	3.194(11)

Bonds NH₄BF₄(IV)	Angle (degrees)	Distance (Å)
N–H₁–F₁	148.7	2.90
N–H₁–F₂	93.67	3.19
N–H₁–F₃	106.78	2.92
N–H₂–F₁	123.8	3.67
N–H₂–F₂	171.4	2.93
N–H₂–F₃	99.0	2.92
	69.9	2.92
N–H₃–F₁	77.9	3.19
N–H₃–F₂	126.6	3.04
N–H₃–F₃	124.0	2.92

mechanism very similar to that proposed for the ammonium halides. This is strongly supported by the observation of localized hydrogen atoms which indicates a change in the rotational motion of the ammonium ion at the transition temperature. It probably changes from a state of unrestricted rotational motion in a symmetrical force field to restrained motion in a less symmetrical force field.

The weak appearance of v_1^+ in the infrared spectrum below 173°K (23) indicates slight distortion of the ammonium ion or the force field surrounding each ammonium ion. The fact that this band is not temperature dependent up to 100°K shows that the distortion cannot possibly be caused by a single strong hydrogen bond, but rather by a series of weak, alternating hydrogen bonds which nicely fits the X-ray data.

It is impossible to make any further deductions regarding the type of motion (i.e., rotation about a 3- or 2-fold axis, etc. (see article by Levy and Peterson (29)) executed by the ammonium ion in NH₄BF₄(IV). Further X-ray work at temperatures below 100°K may prove helpful in this respect.

It is, however, interesting to note that the stability region of NH₄BF₄(IV) appears to be terminated at comparatively low pressures (ca. 3 kbar) (15). This suggests that NH₄BF₄(IV) may be merely an intervening phase between phases III and V (below 80°K (22)) stabilized by the interplay between thermal disorder, on the one hand, and the geometrical distortion caused by the tendency towards hydrogen bonding, on the other. Above 3 kbar the direct III/V transition appears to occur (15).

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