

# The Crystal Structure of the High-temperature Phases of Ammonium and Potassium Tetrafluoroborate

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An approximate model of the crystal structures of the high-temperature phases of ammonium and potassium tetrafluoroborate is presented. The anions are distributed between two sets of statistically equivalent orientations in the frame of the positive ions, resembling that proposed for univalent metal perchlorates. X-Ray diffraction and transition entropy data are interpreted in terms of this model.

Crystalline ammonium and potassium tetrafluoroborate transform from a structurally ordered, orthorhombic room temperature form to a disordered, facecentred, cubic high-temperature structure at elevated temperatures (Table 1). The various phases are closely related to those of the univalent metal perchlorates.<sup>2,11</sup>

Detailed crystal structures of the room-temperature forms have recently been reported.<sup>11-13</sup>

(The two published crystal structures of  $\text{KBF}_4$  are, however, referred to significantly different unit cell dimensions.)  $\text{NaBF}_4$  is reported to change into a hexagonal structure<sup>1</sup> and possibly into a cubic<sup>2</sup> phase on further heating. No second transition was, however, apparent from drop calorimetric measurements.<sup>6</sup> The crystal system of the high-temperature phases of the other alkali metal tetrafluoroborates has not yet been determined.

The published values of the transition temperature of  $\text{NH}_4\text{BF}_4$  (Table 1), show a considerable variation (disregarding the value quoted in Ref. 4 which is almost certainly wrong, as are probably the transition heats quoted in Ref. 10). Other, reported transition heats are rather close to those of the corresponding perchlorates (Table 1, Ref. 14) (except for  $\text{NaBF}_4$ ), while the transi-

Table 1. Crystallographic data for the high-temperature phases of alkalimetal tetrafluoroborates along with transition temperatures and heats.  $n$  = number of molecules per unit cell,  $\Delta H_t$  = transition heat,  $t_t$  = transition temperature. (The numbers in parentheses are probably erroneous.)

|                         | $\text{NaBF}_4$  | $\text{NH}_4\text{BF}_4$   | $\text{KBF}_4$  | $\text{RbBF}_4$  | $\text{CsBF}_4$  |
|-------------------------|--|--|---|--|--|
| Cryst. syst.            | hex.   | f.c. cubic   | f.c.c.  |  |  |
| Cryst. axes (Å)         | $a(t_{\text{exp}}) = 5.00 \pm 0.02$ <sup>1</sup><br>$c(t_{\text{exp}}) = 7.75 \pm 0.03$  | 7.56, <sup>2</sup> 7.57  | 7.27, <sup>2</sup> 7.35   |  |  |
| $t_{\text{exp}}$ (°C)   | 265 <sup>1</sup>   | 260, <sup>2</sup> 260  | 300, <sup>2</sup> 306   |  |  |
| $n$                     | 2  | 4  | 4   |  |  |
| $t_t$ (°C)              | 238.2 <sup>3</sup><br>240—241 <sup>4</sup><br>246—247 <sup>5</sup><br>238—240 <sup>5</sup><br>243 <sup>6</sup><br>243 <sup>7</sup> | 199.5 <sup>3</sup><br>(236 <sup>4</sup> )<br><br>189 ± 5 <sup>8</sup><br>203 | 278.3 <sup>3</sup><br>276—280 <sup>4</sup><br>278—279 <sup>5</sup><br>278—280 <sup>5</sup><br>283 <sup>6</sup><br>283 <sup>7</sup><br>286 | 250—251 <sup>5</sup><br>245—247 <sup>5</sup><br>243 <sup>6</sup><br>245 <sup>7</sup><br>250 <sup>9</sup> | 169—170 <sup>5</sup><br>166—170 <sup>5</sup><br>170 <sup>6</sup><br>169.5 <sup>7</sup><br>176 <sup>9</sup> |
| $\Delta H_t$ (kcal/mol) | 1.61 <sup>6</sup><br>(0.54 <sup>10</sup> )   | 2.12   | 3.30 <sup>6</sup><br>3.28   | 2.86 <sup>6</sup><br>(1.14 <sup>10</sup> )   | 1.94 <sup>6</sup><br>(0.70 <sup>10</sup> )   |

tion temperatures are somewhat lower than those observed in the perchlorates, indicating that the transitions are very similar. Spectroscopic studies as well as the magnitude of the transition heats indicate that the transitions are of the order-disorder type. Reorientation of the  $\text{BF}_4^-$ -groups has been detected in the room temperature phases and the reorientation rate studied as a function of temperature.<sup>9,15</sup>

Finbak and Hassel<sup>2</sup> assumed the cubic, high-temperature phases of  $\text{NH}_4\text{BF}_4$  and  $\text{KBF}_4$  to be rotationally disordered with the  $\text{BF}_4^-$ -ions rotating about axes parallel to the cubic axes. This was also proposed for the perchlorate ions in the alkali metal perchlorates.<sup>16</sup>

The present model of the structure is based on the Frenkel model of disorder and is closely related to that recently derived for the perchlorates.<sup>14</sup>

## EXPERIMENTAL

Commercially available  $\text{KBF}_4$  and  $\text{NH}_4\text{BF}_4$  (Hopkins and Williams, Ltd.) were used without further purification.

X-Ray and differential scanning calorimetry data were measured as described for the per-

chlorates.<sup>14</sup> The powder samples for X-ray analysis were sealed in pyrex tubes to avoid dissociation of the salts. Structure factor amplitudes, temperatures and heats of transition are listed in Tables 3 and 1, respectively.

## RESULTS AND DISCUSSION

Potassium and nitrogen were assumed to be located at  $(\pm \frac{1}{2}, 0, 0)$ ,  $(0, \pm \frac{1}{2}, 0)$  and  $(0, 0, \pm \frac{1}{2})$  etc.<sup>2,14</sup> The various orientations of the anion shown in Fig. 3, Ref. 14, were considered as possible equilibrium positions in a similar way to that described previously.<sup>14</sup> This showed A and B to be the more likely ones at equilibrium. The corresponding statistical fluorine-potassium and fluorine-nitrogen distances are listed in Table 2a, using a fluorine-boron bond length of 1.406(4) Å, which is the average fluorine-boron bond distance observed in  $\text{NH}_4\text{BF}_4$  at room temperature, after correcting for effects of librational motion (e.s.d. in parenthesis).<sup>13</sup> The fluorine-potassium (nitrogen) distances are somewhat shorter than the average fluorine-potassium (nitrogen) distance observed in the ordered room temperature phases<sup>11-13</sup> listed for comparison. This may in part be due to the fact

Table 2. a. Statistical F-K(N) distances (Å) referring to anion position A and B, Fig. 3, Ref. 14, respectively.  $d(\text{B}-\text{F})=1.406$  Å (ass.),<sup>13</sup> symmetry of  $\text{BF}_4^-$ -group: tetrahedral. A is a locked position, B is adjustable by translation along the [111]-direction.

b. Corresponding positional coordinates for the atoms in the  $\text{BF}_4^-$ -group. A: All F-atoms crystallographically equivalent:  $x_B=y_B=z_B=0$ ;  $z_F=0$ . B: three F-atoms crystallographically equivalent:  $x_B=y_B=z_B$ ;  $y_{F_1}=z_{F_1}$ , and  $x_{F_1}=y_{F_1}=z_{F_1}$ .

K(N) in  $(\pm \frac{1}{2}100)$  etc.

| a.<br>Distance                                     | $\text{NH}_4\text{BF}_4$<br>(260 °C) | $\text{KBF}_4$<br>(306 °C) | b.           | $\text{NH}_4\text{BF}_4$<br>(206 °C) | $\text{KBF}_4$<br>(306 °C) |
|--|--------------------------------------|----------------------------|--------------|--------------------------------------|----------------------------|
| A [at (000)]                                       |                                      |                            | A [at (000)] |                                      |                            |
| F(xy0) - Me( $\frac{1}{2}$ 00)                     | 2.76                                 | 2.65                       | $x_F$        | 0.152                                | 0.156                      |
| F(xy0) - Me(0 $\frac{1}{2}$ 0)                     | 3.14                                 | 3.08                       | $y_F$        | 0.107                                | 0.110                      |
| B(000) - Me( $\frac{1}{2}$ 00)                     | 3.783                                | 3.675                      |              |                                      |                            |
| B [at (000)]                                       |                                      |                            | B [at (000)] |                                      |                            |
| F <sub>1</sub> (xyy) - Me( $\frac{1}{2}$ 00)       | 2.83 (ass.)                          | 2.70                       | $x_B$        | -0.038                               | -0.036                     |
| F <sub>2</sub> (xxx) - Me(- $\frac{1}{2}$ 00)      | 3.10                                 | 3.01                       | $x_{F_1}$    | 0.140                                | 0.148                      |
| B(xxx) - Me(- $\frac{1}{2}$ 00)                    | 3.52                                 | 3.43                       | $y_{F_1}$    | -0.074                               | -0.073                     |
| B(xxx) - Me( $\frac{1}{2}$ 00)                     | 4.09                                 | 3.96                       | $x_{F_1}$    | -0.146                               | -0.147                     |
| F - Me (av.) at<br>room temp. (Å) <sup>11-13</sup> | 2.932(0.015)                         |                            |              |                                      |                            |
| Sum of contact<br>radii (Å) <sup>13</sup>          |                                      |                            |              |                                      | 2.69                       |

Table 3. Observed and calculated structure factors based on a combination of A and B. Unobserved and overlapping reflections excluded from  $R$ -value calculations. Overlapping reflections are computed according to  $(\sum pF^2/\sum p/N)^{1/2}$ , where  $p$  denotes the multiplicity of the reflections and  $N$  is the number of overlapping reflections included in the sum. The listed  $F_o$ -values of the non-obs. reflections (n.o.) are computed according to  $I_{n.o.}(hkl) = \frac{1}{2}I_{obs. min.}(hkl)$ .

| $hkl$ | $KBF_4^a$<br>$F_o$ | $F_c$  | $NH_4BF_4^b$<br>$F_o$ | $F_c$  |
|-------|--------------------|--------|-----------------------|--------|
| 1 1 1 | $\leq 7.5$         | 4.36   | 37.4                  | 37.69  |
| 2 0 0 | 96.1               | 92.06  | 60.8                  | 63.18  |
| 2 2 0 | 39.5               | 42.69  | 21.2                  | 26.41  |
| 3 1 1 | 39.7               | -39.97 | 23.6                  | -21.48 |
| 2 2 2 | 28.7               | 32.54  | 18.5                  | 13.60  |
| 4 0 0 | $\leq 22.1$        | 16.42  | 13.4                  | -14.52 |
| 3 3 1 | 20.7               | -22.52 | $\leq 6.0$            | -4.96  |
| 4 2 0 | 19.3               | 13.76  | $\leq 6.2$            | 1.70   |
| 4 2 2 | 20.1               | 18.78  | $\leq 6.9$            | 5.81   |
| 3 3 3 |                    | -2.13  |                       | -2.72  |
| 5 1 1 | $\leq 18.7$        | -11.23 | $\leq 9.1$            | -9.77  |
| 4 4 0 | $\leq 23.8$        | 7.56   | $\leq 11.6$           | -0.08  |
| 5 3 1 | $\leq 12.5$        | -7.99  | $\leq 6.1$            | -1.21  |
| 6 0 0 |                    | 14.60  |                       | 4.16   |
| 4 4 2 | $\leq 22.6$        | 12.91  | $\leq 11.1$           | 6.79   |
| 6 2 0 | $\leq 18.8$        | 8.54   | $\leq 9.2$            | 0.67   |
| 5 3 3 | $\leq 19.3$        | -1.23  | $\leq 9.5$            | 0.31   |
| 6 2 2 | $\leq 19.3$        | 7.25   | $\leq 9.6$            | 1.07   |

<sup>a</sup>  $B(is) = 9.0 \text{ \AA}^2$ ;  $x_A = 0.86$ ;  $R = 0.076$ . <sup>b</sup>  $B(is) = 7.0 \text{ \AA}^2$ ;  $x_A = 0.35$ ;  $R = 0.071$ .

that instantaneous fluorine-potassium (nitrogen) equilibrium separations in the disordered phases are probably on the average somewhat larger than the statistical mean values and that the number of close oxygen-potassium (nitrogen) contacts is smaller in the high-temperature phase. Atomic positional coordinates derived from Table 2a are given in Table 2b.

Structure factors based on anion orientations A and B were calculated using the form factors of Hanson *et al.*<sup>17</sup> and an F-B bond length of 1.382 Å, the mean F-B bond length observed in  $NH_4BF_4$  at room temperature, not corrected for effects of librational effects<sup>18</sup> (e.s.d. in parenthesis). Neutral atoms were assumed for simplicity. A linear combination of the structure factors of A and B was refined by L. S. methods as outlined previously.<sup>14</sup> Observed and calculated structure factors are listed in Table 3. The fraction of molecules in A-type positions,  $x_A$ , is considerably uncertain because of the limited number of observable reflections. The relatively high  $B$ -values are attributable to large amplitudes of molecular libration and to the circumstance that instantaneous equilibrium positions are distributed statistically about the mean positions.

The weighted  $R$ -value,  $R_w$ , based on the structural combination is much less than the  $R_w$ -values obtained for the individual structures in the case of  $NH_4BF_4$ . For  $KBF_4$ , the A struc-

Table 4. Statistical F-F separations about or less than 2.70 Å between a  $BF_4^-$ -group in either the A- or B-position (S) shown in Fig. 3, Ref. 14, and neighbouring  $BF_4^-$ -groups in either A- or B-type orientations (L). Basic positional coordinates in Table 2b.

| Positions   |   | $NH_4BF_4$<br>$d$ (Å) | $KBF_4$<br>$d$ (Å) |
|---|---|-----------------------|--------------------|
| S   | L |                       |                    |
| A   | A |                       |                    |
| $F(xy0) - F(\frac{1}{2} - x, \frac{1}{2} - y, 0)$       |   | 2.65                  | 2.47               |
| $F(xy0) - F(\frac{1}{2} - y, \frac{1}{2} - x, 0)$       |   | 2.61                  | 2.43               |
| A   | B |                       |                    |
| $F(xy0) - F_1(\frac{1}{2} + y, \frac{1}{2} - x, y)$     |   |                       | 2.72               |
| $F(xy0) - F_2(\frac{1}{2} + x, \frac{1}{2} + x, x)$     |   | 2.69                  | 2.54               |
| $F(xy0) - F_3(\frac{1}{2} + x, \frac{1}{2} + x, x)$     |   | 2.69                  | 2.54               |
| B   | B |                       |                    |
| $F_1(xyy) - F_1(\frac{1}{2} + x, x, -\frac{1}{2} - x)$  |   | 2.75                  | 2.61               |
| $F_1(xyy) - F_2(\frac{1}{2} + x, -\frac{1}{2} - x, x)$  |   | 2.75                  | 2.61               |
| $F_2(xxx) - F_3(-\frac{1}{2} - x, -\frac{1}{2} - x, x)$ |   | 2.26                  | 2.15               |

Table 5. The number of orientations of neighbouring  $\text{BF}_4^-$ -groups (L) situated less than 2.70 Å from a given  $\text{BF}_4^-$ -group (S) in either position A or B, shown in Fig. 3, Ref. 14, listed as a function of the corresponding lattice sites associated with L. Derived from Table 4, using the symmetry operations of the space group ( $Fm\bar{3}m$ ). The numbers marked with an asterisk represent F—F distances close to 2.70 Å (2.69 Å, Table 4).

| S (at (000)) | L      | $(\frac{1}{2}\frac{1}{2}0)$ | $(0\frac{1}{2}\frac{1}{2})$ | $(\frac{1}{2}0\frac{1}{2})$ | $(\frac{1}{2}\frac{1}{2}\bar{0})$ | $(0\frac{1}{2}\frac{1}{2}\bar{1})$ | $(\frac{1}{2}0\frac{1}{2}\bar{1})$ | $(\frac{1}{2}\frac{1}{2}0\bar{1})$ | $(\frac{1}{2}\frac{1}{2}\bar{1}0)$ | $(\frac{1}{2}\frac{1}{2}\bar{1}\bar{1})$ | $(\frac{1}{2}0\frac{1}{2}\bar{1}\bar{1})$ | $(\frac{1}{2}\bar{1}\bar{1}0)$ |                          |
|--------------|--------|-----------------------------|-----------------------------|-----------------------------|-----------------------------------|------------------------------------|------------------------------------|------------------------------------|------------------------------------|--|---|--------------------------------|--------------------------|
| A            | A-type | 2                           |                             |                             |                                   |                                    | 2                                  | 2                                  |                                    | 2  |   | $\text{NH}_4\text{BF}_4$       |                          |
|              | »      | 2                           |                             |                             |                                   |                                    | 2                                  | 2                                  |                                    | 2  |   | $\text{KBF}_4$                 |                          |
| A            | B-type | 2*                          |                             |                             |                                   |                                    | 2*                                 | 2*                                 |                                    | 2*                                       |   | $\text{NH}_4\text{BF}_4$       |                          |
|              | »      | 2                           |                             |                             |                                   |                                    | 2                                  | 2                                  |                                    | 2  |   | $\text{KBF}_4$                 |                          |
| B            | A-type |                             |                             |                             |                                   |                                    |                                    |                                    |                                    | 2*                                       | 2*  | 2*                             | $\text{NH}_4\text{BF}_4$ |
|              | »      |                             |                             |                             |                                   |                                    |                                    |                                    |                                    | 2  | 2   | 2                              | $\text{KBF}_4$           |
| B            | B-type |                             |                             |                             |                                   |                                    |                                    |                                    |                                    | 1  | 1   | 1                              | $\text{NH}_4\text{BF}_4$ |
|              | »      |                             |                             |                             | 1                                 | 1                                  | 1                                  | 1                                  | 1                                  | 1  | 3   | 3                              | $\text{KBF}_4$           |

ture is found to dominate in the combination, leading to an  $R_w$ -value, which is only 5–6 % less than that based on pure A structure.

The van der Waals radius of fluorine is reported as 1.35 Å.<sup>18</sup> Empirical values of the ionic radius are 1.36 Å<sup>18</sup> and 1.33 Å,<sup>19</sup> while a calculated value is 1.40 Å.<sup>20</sup> The minimum, equilibrium intermolecular F—F separation<sup>14</sup> was chosen as 2.70 Å in the present case. (The shortest intermolecular F—F distance in the room temperature phases is much larger than this value.<sup>11–13</sup>) Statistical, intermolecular F—F separations equal to or less than 2.70 Å calculated for the high-temperature phases, are listed in Table 4. The number of neighbouring anions situated less than 2.70 Å from a chosen  $\text{BF}_4^-$ -group in either the A or B position in Fig. 3, Ref. 14, is listed as a function of the associated lattice sites in Table 5. The configurational entropies ( $S_c$ ) were computed as described for the perchlorates,<sup>14</sup> using the results of Tables 3 and 5, etc.<sup>14</sup> This gave:

$S_c = 4.40$  cal/mol K and  $S_c = 2.93$  cal/mol K, for  $\text{NH}_4\text{BF}_4$  and  $\text{KBF}_4$ , respectively, while the transition entropies, obtained as  $\Delta H_t/T_t$ , from Table 1, are

$\Delta S_t = 4.45$  cal/mol K and  $\Delta S_t = 5.85$  cal/mol K, respectively. The  $S_c$ -values suffer from inaccuracy in the basic  $x_A$ -values noted above, in addition to the general uncertainty associated with the evaluation of the configurational entropy discussed in Ref. 14. Thus ignoring the numbers marked with an asterisk in Table 4 in the calculations,<sup>14</sup> leads to an  $S_c$ -value of 4.89

cal/mol K for  $\text{NH}_4\text{BF}_4$ , which is even greater than the experimental transition entropy. The findings indicate, however, that the presence of the  $\text{NH}_4^+$ -ion does not give rise to a particularly large contribution to the transition entropy, as also noted for  $\text{NH}_4\text{ClO}_4$ .<sup>14</sup>

The transition entropies observed in  $\text{KClO}_4$ <sup>14</sup> and  $\text{KBF}_4$  are particularly high. Comparison with the results obtained for  $\text{KClO}_4$  indicates that the  $x_A$ -value obtained for  $\text{KBF}_4$  may be too high and the  $S_c$ -value correspondingly too low. Inspection shows, however, that the discrepancy between  $\Delta S_t$  and  $S_c$  is rather large, irrespectively of the  $x_A$ -value. A similar result was also obtained for  $\text{KClO}_4$ . A specific explanation of these relatively large discrepancies has not been found. In general, the difference between observed transition entropies and calculated configurational entropies is ascribed to various factors, such as changes in the vibrational state associated with the transition<sup>21,22</sup> as well as additional (orientational or positional) disorder in the high-temperature phases.<sup>14</sup>

The present high-temperature phases are apparently very similar to those of the corresponding perchlorates. Much of the discussion in Ref. 14 is thus equally valid here. Comparison of Table 1 and Table 1, Ref. 14, indicates that the high-temperature forms of  $\text{RbBF}_4$  and  $\text{CsBF}_4$  may have crystal structures similar to those of the perchlorates.<sup>14</sup>

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