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The Crystal Structure of Ammonium Heptafluorozirconate and the Disorder of the Heptafluorozirconate Ion

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In an X-ray diffraction study of ammonium heptafluorozirconate, $(NH_4)_3ZrF_7$, the disordered fluorine scattering density distribution has been determined. A disordered ZrF_7^{3-} ion, in the shape of a pentagonal bipyramid, and with reasonable dimensions, can be fitted into this distribution. Apparent hydrogen electron density in difference syntheses suggests the presence of N–H···F hydrogen bonds which are formed and broken during the ionic reorientations, together with some disorder of the ammonium ions. The final discrepancy index $R=\sum(|F_o|-|F_c|)/\sum|F_o|$ is 0·023.

Introduction

Ammonium fluorozirconates are useful in the electrolytic recovery of zirconium (Hull & Turnbull, 1967). Our interest in the substance ammonium heptafluorozirconate, $(NH_4)_3ZrF_7$, arose in connexion with nuclear magnetic resonance studies being made in this Division.

This substance is unusual because the ZrF_7^{3-} ion, if it exists, must be fitted into a face-centred cubic lattice. Work published to date on $(NH_4)_3ZrF_7$ suggests that the ion exists and is highly disordered; however the geometry of the ion and the nature of the disorder have so far not been experimentally determined.

The original model of Hassel & Mark (1924), consisting of ZrF_6^{2-} ions and F^- ions, was shown to have impossibly small contact distances by Hampson & Pauling (1938). Hampson & Pauling pointed out that space group theory provided no way of placing an ordered ZrF_7^{3-} ion in the cubic lattice. They proposed instead a model containing a ZrF_7^{3-} ion with C_{3v} symmetry (a capped octahedron) in the space group $Fm3m$, which was disordered so that its threefold axis was parallel with any of the eight [111] directions, giving 16 possible orientations of the ZrF_7^{3-} ion. Some disorder of the zirconium and nitrogen atoms was also postulated.

Further evidence for the existence of the ZrF_7^{3-} ion in $(NH_4)_3ZrF_7$ relates to the fact that K_3UF_7 exists in an ordered tetragonal form and a disordered cubic form. Zachariasen (1954) has deduced that the tetragonal structure contains pentagonal bipyramidal UF_7^{3-} ions, and he has proposed a structure for the disordered form which also contains such ions. He then concludes that $(NH_4)_3ZrF_7$ and K_3UF_7 are isostructural.

The geometry of the NbF_7^{2-} ion in K_2NbF_7 is well known. The structure was first solved by Hoard (1939) and later refined by neutron diffraction (Brown & Walker, 1966). The structure is ordered and the seven fluorine atoms are crystallographically independent. The NbF_7^{2-} ion in K_2NbF_7 is a slightly distorted capped trigonal prism.

The present X-ray analysis of $(NH_4)_3ZrF_7$ was undertaken with the aim of determining the geometry of the ZrF_7^{3-} ion in this crystal and the nature of its disorder.

Experimental

Crystals showing octahedral faces were grown by the method of de Boer & van Arkel (1924). An X-ray powder photograph taken with a Philips 114·6 mm diameter camera gave a face-centred cubic pattern with $a = 9{\cdot}419 \pm 0{\cdot}001$ Å, in agreement with the value of 9·417 Å given by Swanson, Gilfrich & Cook (1956). The X-ray density is 2·21 g.cm^{-3}, for four formula units in the unit cell, agreeing with measured densities of 2·20 g.cm^{-3} (Hassel & Mark, 1924) and 2·196–2·205 g.cm^{-3} (von Hevesy, 1926).

X-ray diffraction data were collected using a General Electric XRD-5 X-ray set and single-crystal orienter. For maximum accuracy, the single crystal used was ground to a sphere of radius $r = 0{\cdot}0130 \pm 0{\cdot}0020$ cm, by shaking it in a pill pack lined with emery paper. The crystal was mounted on a glass fibre and covered with a thin film of silicone grease to prevent decomposition. Complete data were collected with Zr-filtered Mo $K\alpha$ radiation to $2\theta = 54°$, comprising 78 independent reflexions. Each reflexion was measured in two different octants of reciprocal space. The linear absorption coefficient μ, for Mo $K\alpha$ is 15 cm^{-1}, giving $\mu r = 0{\cdot}195$. The need for absorption corrections was thus eliminated, as the variation of the transmission factor over the 2θ range was negligible. The observed intensities, Q_{hkl}, with background B_{hkl} subtracted, were converted to structure factors F_{hkl} with the program *CDRABS* (A.A.E.C. neutron diffraction program library). Standard deviations were assigned to the Q_{hkl} values according to the formula

$$\sigma^2(Q) = \sigma_1^2(Q) + \sigma_2^2(Q)$$

where

$$\sigma_1(Q) = (Q + 2B)^{1/2}$$

is the statistical error and

$$\sigma_2(Q) = \alpha + \beta Q$$

allows for other errors such as the errors in estimating the B_{hkl}, variations in tube output, *etc.* The constant α was taken as the minimum observable intensity, 500, and β was taken as 0·05. There were no unobserved intensities in the range of the data. Standard deviations in F_{hkl} were calculated by *CDRABS* to give weighting factors

$$w_{hkl} = 1/\sigma^2(F_{hkl})$$

which were used in the least-squares refinement below.

Determination of the structure

The four zirconium atoms in the unit cell occur in positions 4(*a*) of space group *Fm*3*m*. The vectors involving the zirconium atom should therefore lie at the atomic positions in the Patterson function, which is in this case a map roughly resembling the structure. The zero layer of the three-dimensional Patterson function is shown in Fig. 1. Two peaks appeared to be Zr–F vectors; vector (1), 1·96 Å from the origin, and vector (2), 2·16 Å from the origin. The shape and nature of the ZrF_7^{3-} ion was not apparent from these diffuse peaks. Vectors at $(0,0,\frac{1}{2})$ and $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ were assumed to be the Zr–N(1) and Zr–N(2) vectors. The data thus could not be analysed in terms of ordered fluorine atoms. The disordered fluorine electron density distribution was

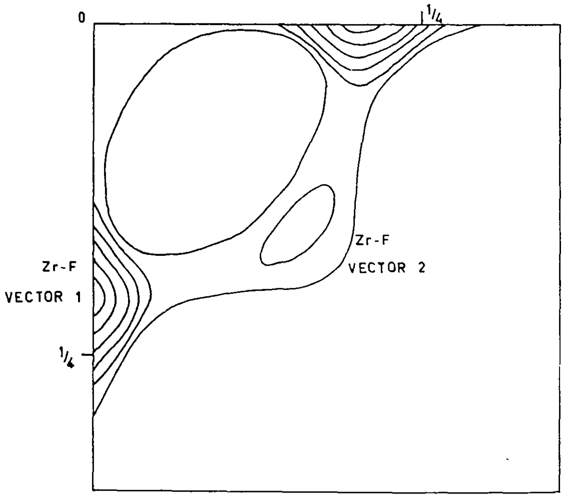

Fig. 1. Zero layer of the three-dimensional Patterson synthesis, showing the Zr–F(1) (vector 1) and Zr–F(2) (vector 2) vectors. Contours arbitrary.

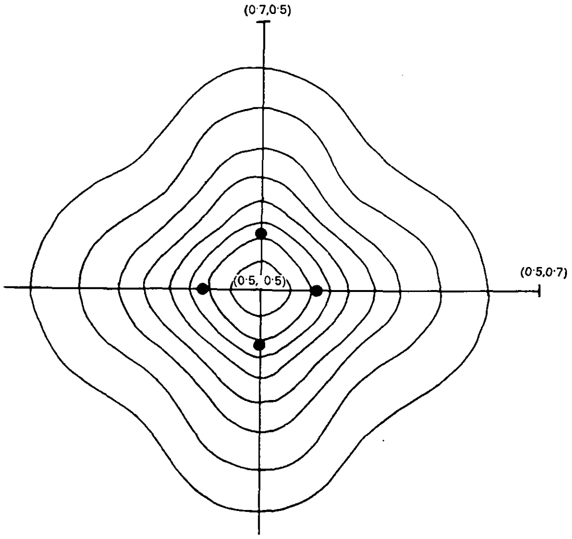

Fig. 2. Section through $Z = 0{\cdot}209$ of the difference Fourier synthesis obtained by leaving out F(1) from the calculated structure factors. Contours 0, 150, 300, . . ., 1050 are in arbitrary units. The disordered F(1) sites as refined by least-squares are shown by black dots.

accounted for in the calculated structure factors by placing partial fluorine 'atoms' within the disorder peaks in such a way that the observed peak shapes were reproduced. The positional and thermal parameters of these 'atoms' were refined in the usual way with the least-squares program *ORFLS* (Busing, Martin & Levy, 1962*a*). Difference syntheses were used to check the fit between the observed and calculated fluorine distributions.

Vector (1) was accounted for by four partial fluorine atoms F(1) in positions 96(*j*) of space group *Fm*3*m*, and vector (2) was accounted for by two partial fluorine atoms F(2), also in positions 96(*j*). The partial fluorine atom arrangement is shown in Figs. 2 and 3. From an initial value of $R_1=\sum(|F_o|-|F_c|)/\sum|F_o|$ of 0·30, isotropic least-squares refinement led to $R_1=0{\cdot}036$ and anisotropic refinement to $R_1=0{\cdot}031$. The X-ray scattering curves used were for neutral atoms (*International Tables for X-ray Crystallography*, 1962, p. 202 and 211), with the zirconium curve corrected for the anomalous dispersion term $\Delta f'=-2{\cdot}8\ e$ (*International Tables for X-ray Crystallography*, 1962, p. 216). The term $\Delta f''=0{\cdot}8\ e$ was neglected.

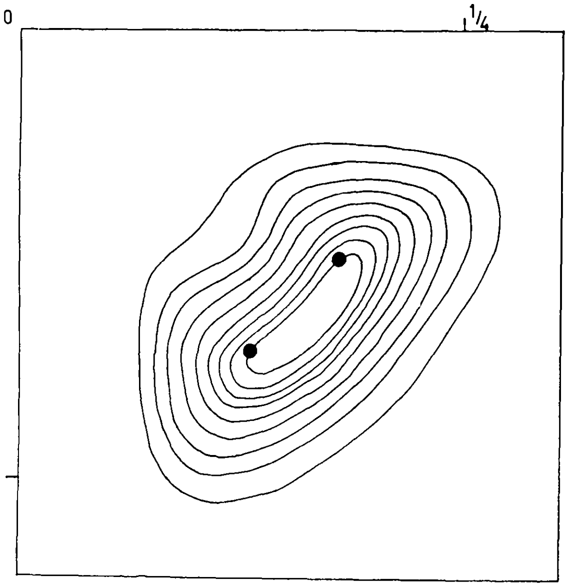

Fig. 3. Section through $Z=0$ of the difference Fourier synthesis obtained by leaving out F(2) from the calculated structure factors. Contours 0, 25, 50, ..., 200 units, on the same scale as in Fig. 2. The disordered F(2) sites as refined by least-squares are shown by black dots.

Difference maps at this stage gave peaks which seemed to represent hydrogen electron density. N(1) at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ was surrounded octahedrally by six peaks H(1) at $(\frac{1}{2},\frac{1}{2},0{\cdot}4)$ *etc.*, and the N(1)–H(1) vectors pointed in the direction of F(1). The fact that there were six peaks instead of four was evidence of disorder in this NH_4^+ ion. There were four peaks H(2) around N(2) at (0·2,0·2,0·2), *etc.*, such that the N(2)–H(2) vectors pointed in the direction of F(2). The hydrogen coordinates and the thermal parameters of H(2) were refined with *ORFLS*; however, the thermal parameters of H(1) were not physically sensible. Both hydrogen atoms were then given isotropic Debye–Waller temperature factors of 4·0 Å², which were not varied. This hydrogen atom assignment was regarded as tentative only, but it was considered that the hydrogen atoms were in the correct region of the unit cell. Final discrepancy factors including the hydrogen atoms were $R_1=0{\cdot}023$ and

$$R_2=[\sum w(F_o-F_c)^2]^{1/2}/(\sum wF_o^2)^{1/2}=0{\cdot}027\,.$$

In the above refinement, the partial fluorine atom sites F(1) and F(2) were assigned occupancy factors of $20{\cdot}8\,{}^0/_0$ and $8{\cdot}3\,{}^0/_0$ on the basis of Fourier peak weights. These multipliers did not alter significantly when they were allowed to refine at the conclusion of the least-squares analysis.

A difference synthesis at the end of the refinement showed no undesirable features. The final positional and thermal parameters are given in Table 1. The partial fluorine temperature factors in Table 1 have no meaning in terms of the vibration parameters of individual fluorine atoms. Distances and angles calculated with the program *ORFFE* (Busing, Martin & Levy, 1962*b*) are given in Table 2, and the final observed and calculated structure factors with $\sigma(F_o)$ values in Table 3.

Structure factors were calculated leaving out F(1) ($R_1=0{\cdot}18$) and F(2) ($R_1=0{\cdot}05$) and these structure factors gave difference electron density maps of the F(1) and F(2) distributions as shown in Figs. 2 and 3.

Fig. 4 shows the F(1) and F(2) sites surrounding one zirconium atom. It is of interest that a solution, but not a unique one, to the problem of the ZrF_7^{3-} ion geometry and disorder can be obtained directly from the partial fluorine atom distribution. A slightly distorted

Table 1. *Final positional and anisotropic thermal parameters in* $(NH_4)_3ZrF_7$*

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zr	0	0	0	0·0058 (1)	0·0058 (1)	0·0058 (1)	0	0	0
F(1)	0	0·0383 (18)	0·2086 (5)	0·0154 (14)	0·0655 (49)	0·0046 (5)	0	0	0·0010 (15)
F(2)	0	0·1297 (27)	0·1771 (22)	0·0121 (27)	0·0427 (104)	0·0107 (26)	0	0	−0·0131 (50)
N(1)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0·0120 (7)	0·0120 (7)	0·0120 (7)	0	0	0
N(2)	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0·0126 (5)	0·0126 (5)	0·0126 (5)	0	0	0
H(1)	0	0	0·402 (20)	0·0113	0·0113	0·0113	0	0	0
H(2)	0·205 (20)	0·205 (20)	0·205 (20)	0·0113	0·0113	0·0113	0	0	0

* The temperature factor is $\exp\,[-(\beta_{11}h^2+2\beta_{12}hk+\ldots)]$.

Table 2. *Distances and angles in* (NH$_4$)$_3$ZrF$_7$

ZrF$_7^{3-}$ ion*

Lengths†		Angles	
Zr–F(1)	2·00 (1) Å		
Zr–F(2)	2·07 (2)		
A–C	2·78 (1)	*A*–Zr–*C*	88·1 (2)°
A–D	2·78 (1)	*A*–Zr–*D*	88·1 (2)
A–E	2·82 (1)	*A*–Zr–*E*	90·0
A–F	3·08 (1)	*A*–Zr–*F*	98·4 (4)
A–G	3·08 (1)	*A*–Zr–*G*	98·4 (4)
B–C	2·87 (1)	*B*–Zr–*C*	91·9 (2)
B–D	2·87 (1)	*B*–Zr–*D*	91·9 (2)
B–E	2·82 (1)	*B*–Zr–*E*	90·0
B–F	2·65 (2)	*B*–Zr–*F*	81·6 (4)
B–G	2·65 (2)	*B*–Zr–*G*	81·6 (4)
C–E	2·56 (1)	*C*–Zr–*E*	79·8 (4)
E–D	2·56 (1)	*E*–Zr–*D*	79·8 (4)
D–G	2·15 (3)	*D*–Zr–*G*	64·2 (12)
G–F	2·44 (5)	*G*–Zr–*F*	72·4 (16)
F–C	2·15 (3)	*F*–Zr–*C*	64·2 (12)

Hydrogen bonds

Lengths†		Angles	
N(1)–F(1)	2·77 (1) Å		
N(2)–F(2)	2·70 (1)		
N(1)–H(1)	0·93 (20)	N(1)–H(1)···F(1)	169 ± 25°
N(2)–H(2)	0·73 (20)	N(2)–H(2)···F(2)	144 ± 25

* The F(1) positions *ABCDE* and the F(2) positions *F* and *G* are derived from the coordinates in Table 1 by the symmetry transformations given in Table 4.

† Uncorrected for thermal motion.

Table 3. *Observed and calculated structure factors together with σ(F$_o$) values*

H	K	L	FO	FC	σ(FO)
0	2	0	153.89	147.39	3.8
0	4	0	216.44	218.38	5.4
0	6	0	103.45	105.73	2.2
0	8	0	69.83	67.48	2.0
0	10	0	51.55	52.66	1.2
0	12	0	24.45	24.36	1.2
0	6	2	95.35	93.09	2.1
0	8	2	39.74	39.33	1.0
0	10	2	49.28	49.50	1.2
0	12	2	16.60	17.40	1.4
1	1	1	161.44	158.01	3.7
1	3	1	63.87	65.99	1.4
1	5	1	118.00	118.73	2.8
1	7	1	42.69	43.25	1.3
1	9	1	51.76	50.96	1.5
1	11	1	28.14	28.64	1.1
2	2	0	139.79	147.78	3.3
2	4	0	91.36	88.32	2.0
2	2	2	10.41	9.85	0.6
2	4	2	117.84	120.32	3.4
2	6	2	53.40	52.14	1.3
2	8	2	49.14	49.30	1.1
2	10	2	37.87	38.60	1.0
2	12	2	22.37	20.29	1.2
3	3	1	47.57	51.98	1.4
3	5	1	78.75	77.20	1.8
3	7	1	35.17	35.67	1.0
3	9	1	42.83	41.85	1.1
3	11	1	24.58	24.33	1.1
3	3	3	64.19	66.78	1.6
3	5	3	72.94	72.13	1.8
3	7	3	39.85	39.38	1.0
3	9	3	42.19	41.02	1.1
3	11	3	22.77	23.61	1.6
4	4	0	122.04	121.18	2.9
4	6	0	60.87	60.64	1.4
4	8	0	52.98	52.39	1.2
4	0	0	34.61	36.02	1.0
4	4	2	81.11	79.61	1.9
4	6	2	73.73	73.63	1.9
4	8	2	41.48	41.33	1.1
4	10	2	40.01	39.99	1.1
4	4	4	92.41	90.56	2.2
4	6	4	46.32	46.61	1.1
4	8	4	48.41	47.45	1.2
4	10	4	28.34	28.39	1.1
5	5	1	76.71	75.85	1.9
5	7	1	45.55	45.32	1.1
5	9	1	38.87	38.42	1.0
5	11	1	22.64	23.72	1.2
5	5	3	58.42	56.45	1.4
5	7	3	41.93	41.44	1.1
5	9	3	35.21	33.74	1.5
5	11	3	19.03	21.18	1.3
5	5	5	45.63	45.44	1.1
5	7	5	37.61	35.66	1.0
5	9	5	28.21	27.31	1.1
6	6	0	63.03	65.32	1.5
6	8	0	33.47	34.58	1.0
6	10	0	32.67	33.29	1.0
6	6	2	44.39	45.30	1.1
6	8	2	40.82	41.07	1.1
6	10	2	25.96	26.36	1.1
6	6	4	48.82	48.37	1.1
6	8	4	29.96	30.65	1.0
6	10	4	25.22	26.00	1.2
6	6	6	35.62	34.54	1.0
6	8	6	31.73	31.31	1.1
7	7	1	30.54	30.80	1.0
7	9	1	23.92	25.92	1.1
7	7	3	30.17	30.08	1.0
7	9	3	25.84	24.83	1.6
7	7	5	29.95	29.92	1.1
7	9	5	22.09	21.69	1.2
7	7	7	24.50	24.05	1.2
8	8	0	28.22	29.62	1.1
8	8	2	23.56	24.51	1.1
8	8	4	29.11	28.41	1.1

pentagonal bipyramidal ion with reasonable dimensions (Table 2) was constructed as shown in Fig. 4. It could only be obtained using five F(1) sites and two F(2) sites, in agreement with the relative weights of the F(1) and F(2) Fourier peaks of 5:1. There were 24 equivalent orientations of this ion. This solution is considered, together with other possible interpretations of the disordered fluorine density, in the *Discussion* below.

Discussion

The disordered ZrF$_7^{3-}$ *ion*

As mentioned above, a slightly distorted pentagonal bipyramid can be fitted into the F(1) and F(2) partial fluorine atom sites. In Fig. 4, this ion is denoted by [Zr, *A*, *B*, *C*, *D*, *E*, *F*, *G*] where *A*, *B*, *C*, *D*, and *E* are F(1) sites and *F* and *G* are F(2) sites. The atoms forming the pentagon are *C*, *D*, *E*, *F* and *G*. The sites *A–G* for this orientation are obtained by operating on the basic coordinates for F(1) and F(2) in Table 1, according to the scheme in Table 4.

The interatomic distances and angles in this ZrF$_7^{3-}$ ion are given in Table 2. The Zr–F(1) and Zr–F(2) distances are 2·00 and 2·07 Å, the F–Zr–F angles vary from 64 to 98°, and the F–F distances vary from 2·16 to 3·08 Å. For comparison, the Nb–F distances in the NbF$_7^{2-}$ ion as found by neutron diffraction (Brown & Walker, 1966) vary from 1·94 to 1·98 Å, the F–Nb–F angles vary from 74 to 98° and the F–F distances vary from 2·36 to 2·91 Å. The dimensions of this hypothetical ZrF$_7^{3-}$ ion are thus quite reasonable. Distortions of this basic ion are also possible by choosing alternative F(1) sites, but it is always necessary initially to choose two adjacent F(2) sites, before adding F(1) sites. Only small distortions of the ion shown in Fig. 4 are needed to give a regular pentagonal bipyramid. It is conceivable that a regular ion exists in the crystal, in a whole spectrum of orientations, within the limits of the fluorine density distribution.

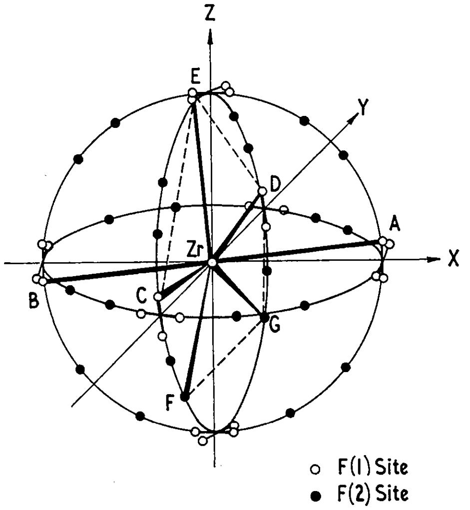

Fig. 4. Distribution of disordered fluorine atoms around the zirconium atom. The open circles are F(1) sites, and the shaded circles are F(2) sites. A possible orientation of a disordered pentagonal bipyramidal ZrF$_7^{3-}$ ion, as discussed in the text, is shown.

Table 4. *Derivation of pentagonal bipyramidal* ZrF_7^{3-} *ion*

Disordered fluorine site	Type	Symmetry operation on basic coordinate (x,y,z) in Table 1		
A (on pentagonal axis)	F(1)	z	x	y
B (on pentagonal axis)	F(1)	$-z$	x	$-y$
C (in pentagon)	F(1)	x	$-z$	y
D (in pentagon)	F(1)	x	z	y
E (in pentagon)	F(1)	$-y$	x	z
F (in pentagon)	F(2)	x	$-y$	$-z$
G (in pentagon)	F(2)	x	y	$-z$

The capped octahedron model (C_{3v} symmetry) of Hampson & Pauling (1938) is eliminated by the observed fluorine distribution, as it requires fluorine density along the [111] axis, whereas none is observed. The bipyramidal ZrF_7^{3-} ion, as oriented in the model of Zachariasen (1954), does not fit fully within the observed fluorine density distribution. We have not been able to fit a capped trigonal prism arrangement in the fluorine distribution, as occurs in K_2NbF_7 (Brown & Walker, 1966; Hoard, 1939).

The above analysis has shown that it is reasonable to inscribe a regular, or near regular, disordered pentagonal bipyramidal ion in the fluorine density distribution. It is impossible to determine accurately the dimensions of the ZrF_7^{3-} ion in $(NH_4)_3ZrF_7$ in a room-temperature diffraction experiment. A similar situation occurs in the case of IF_7 (Donohue, 1965), where it is impossible with the X-ray diffraction data to demonstrate that the symmetry of the IF_7 molecule is different from D_{5h}.

Hydrogen bonding

Pintar, Lahajnar & Slivnik (1966) carried out an n.m.r. study of $(NH_4)_3ZrF_7$. Their data indicate slow reorientation of the ZrF_7^{3-} ion and fast reorientation of the NH_4^+ ions, together with probable hydrogen bond formation. The ammonium ion at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$ is certainly disordered, as there is no way of placing an ordered tetrahedral ion at a site with point symmetry *m*3*m*. As mentioned above, difference syntheses gave an octahedral arrangement of hydrogen electron density around N(1) into which disordered $(NH_4)^+$ tetrahedra are presumably fitted. A tetrahedral distribution was found about N(2). The N–F distances and N–H$\cdots$F angles in Table 2 suggest that hydrogen bonds are formed and broken in the ZrF_7^{3-} and NH_4^+ ion reorientations. As hydrogen makes only a small contribution to the diffracted intensities, no further interpretation of the hydrogen peaks in terms of ammonium tetrahedra is possible. A neutron diffraction study of ammonium heptafluorozirconate has been commenced in order to elucidate the role of the ammonium ions in this compound.

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