A neutron diffraction analysis of the disorder in ammonium heptafluorozirconate. By H. J. Hurst and J. C.

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A neutron diffraction study of $(NH_4)_3ZrF_7$ has confirmed the disorder of the ZrF_7^{3-} ion and the ammonium ions at room temperature. The probable configuration of the ZrF_7^{3-} ion is a pentagonal bipyramid. The $(NH_4)^I$ and $(NH_4)^{II}$ ions are dynamically disordered and involved in hydrogen bonding.

Introduction

An X-ray crystal structure analysis of $(NH_4)_3ZrF_7$, which is cubic with space group $Fm3m$ and $a_0 = 9.419 \pm 0.001$ Å, has shown that the fluorine density distribution is disordered and that the probable configuration of the ZrF_7^{3-} ion is pentagonal bipyramidal (Hurst & Taylor, 1970). Nuclear magnetic resonance studies have shown that the ZrF_7^{3-} ions and NH_4^+ ions in $(NH_4)_3ZrF_7$ are dynamically disordered and reorienting (Blinc & Lahajnar, 1967; Pintar, Lahajnar & Slivnik, 1966). The present neutron study was begun to determine the nature of the disorder of the ammonium ions.

Experimental and analysis

Large single-crystals with {111} faces were grown by the method of de Boer & van Arkel (1924). The crystal used was ground to a cylinder of diameter 0.57 cm and length 0.32 cm, the cylinder axis being along [111]. The neutron diffraction data were collected at room temperature on the automatic diffractometer on HIFAR, the A.A.E.C. research reactor (Pryor, Ellis & Dullow, 1968). Complete data to $2\theta = 100°$ ($\lambda = 1.17$ Å) were collected, comprising 50 independent observed reflexions and 26 independent unobserved reflexions. The 13 strongest reflexions were measured in three octants of reciprocal space, 12 reflexions of medium intensity in two octants, while the remaining weak and unobserved reflexions were measured in one octant. The data were corrected for absorption ($\mu_{meas} = 2.4$ cm^{-1}) and converted to structure amplitudes with associated estimated standard deviations by the procedure described in Hurst & Taylor (1970).

Structure factors calculated with the X-ray parameters for F, N and Zr using the program *ORFLS* (Busing, Martin & Levy, 1962) gave $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.29$. The neutron scattering lengths were taken from Bacon (1962). A three-dimensional difference synthesis confirmed the disordered X-ray fluorine distribution and revealed the disordered hydrogen scattering density. A least-squares refinement with unit weights using *ORFLS*, in which the shapes of the disordered atom peaks were accounted for by fractional fluorine and hydrogen atoms, led to the parameters given in Table 1, for which $R = 0.033$. Extinction effects were not large in these data. The observed and calculated structure factors are given in Table 2.

The disorder of $(NH_4)^I$ at $(00\frac{1}{2})$

It is impossible to fit an ordered tetrahedral ion into a location with point symmetry $m3m$. The observed hydrogen scattering density around N(1) consisted of six peaks along [100] axes as shown in Fig. 1(*a*). A similar situation occurs in the NaCl-phase of ND_4Br (Levy & Peterson, 1953). These authors considered eight models for the ammonium ion distribution, of which three gave reasonable agreement with the observed neutron powder patterns. The model (3) of Levy & Peterson (in which two hydrogen atoms were

placed in {100} planes and two hydrogen atoms were placed in {110} planes, so that approach distances to the bromide ions were minimized) was the only model which was in agreement with the distribution of Fig. 1(*a*). A close examination of this figure revealed that the fit of the ammonium ion was improved by:

(*a*) displacing N(1) by about 0.1 Å along [110] directions, as suggested by the high Debye–Waller B value for N(1) of 4.7 Å^2;

(*b*) allowing distortion of the ammonium ion – such as occurs in ammonium sulphate (Schlemper & Hamilton, 1966).

The shapes of the peaks in Fig. 1(*a*) were accounted for in the calculations by a static model involving fractional hydrogen atoms H_{0yz} with occupancy factors of 16.7%, in positions 96(*j*) of $Fm3m$ (see Table 1). Since the distance N(1)–F(1) is 2.80 (1) Å with an angle N(1)–H_{0yz}...F(1) of 167°, hydrogen bonds are probably formed and broken in the reorientations. The N(1)–H_{0yz} distance is 1.07 Å.

The NaCl-phase of NH_4I has recently been studied with neutron diffraction by Seymour & Pryor (1970). The hydrogen distribution found in NH_4I was similar to that shown in Fig. 1(*a*) and was described by Kubic Harmonic functions.

The disorder of $(NH_4)^{II}$ at $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$

N(2), with a B of 4.2 Å^2, is surrounded by four hydrogen peaks on the [111] axes. These peaks are broad as shown in Fig. 1(*b*) and (*c*), which are two sections perpendicular to the threefold axis, 0.17 Å apart. This hydrogen peak shape was accounted for by a static distribution of fractional hydrogen atoms H_{xzz} in 96(*k*) and H_{xyz} in 192(*l*) [see dots in Fig. 1(*b*) and (*c*)].
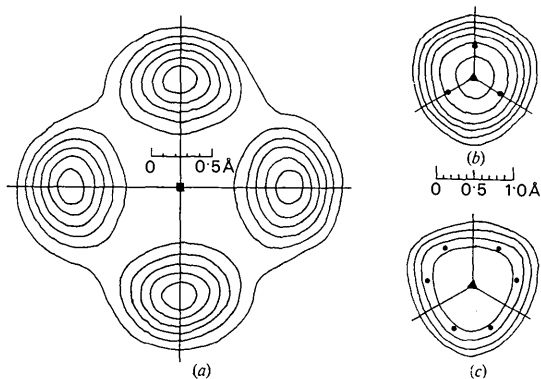
Fig. 1. Hydrogen neutron scattering density distribution for (*a*) $(NH_4)^I$, contours $-10, -20, \ldots$ (*b*) $(NH_4)^{II}$. Section perpendicular to the threefold axis through (0.188, 0.188, 0.188). Contours $-10, -20, \ldots$ Dots indicate H_{xzz} positions. Same scale as (*a*). (*c*) $(NH_4)^{II}$. Section perpendicular to the threefold axis through (0.198, 0.198, 0.198). Dots indicate H_{xyz} positions. Contours $-10, -20, \ldots$

Table 1. *Positional and thermal parameters in* (NH₄)₃ZrF₇*

	Wyckoff notation	% Occupancy	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
F(1)	96(j)	20·8	0	0·0462 (12)	0·2062 (8)	0·0112 (13)	0·0186 (24)	0·0060 (6)	0	0	−0·0014 (8)
F(2)	96(j)	8·3	0	0·1317 (23)	0·1880 (21)	0·0144 (29)	0·0097 (24)	0·0071 (21)	0	0	−0·0024 (23)
H₀ᵧᵤ / H$_{0yz}$	96(j)	16·7	0	0·0329 (22)	0·3914 (15)	0·0107 (28)	0·0089 (24)	0·0164 (17)	0	0	−0·0028 (12)
H$_{xyz}$	192(l)	11·1	0·2342 (57)	0·2104 (73)	0·1560 (54)	0·0148 (109)	0·0082 (81)	0·0179 (31)	0·0040 (55)	0·0023 (20)	−0·0008 (35)
H$_{xzz}$	96(k)	11·1	0·1680 (58)	0·1680	0·2259 (74)	0·0065 (50)	0·0065	0·0133	−0·0022 (52)	−0·0029 (19)	−0·0029
N(1)	4(b)	100·0	0·0000	0·0000	0·5000	0·0133 (4)	0·0133	0·0133	0	0	0
N(2)	8(c)	100·0	0·2500	0·2500	0·2500	0·0118 (3)	0·0118	0·0118	0	0	0
Zr	4(a)	100·0	0	0	0	0·0059 (3)	0·0059	0·0059	0	0	0

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

Table 2. *Observed and calculated structure factors for*
(NH₄)₃ZrF₇

Unobserved reflexions are denoted by asterisks.

H	K	L	|Fo|	Fc	σ(Fo)	H	K	L	|Fo|	Fc	σ(Fo)
0	0	2	6.80	6.80	.13	2	2	4	11.39	11.30	.20
0	0	4	14.05	14.39	.23	2	2	6	2.78	-2.76	.12
0	0	6	1.36	1.34	.20	2	2	8	4.38	4.27	.13
0	0	8	6.38	6.29	.13	2	2	10	1.81	1.69	.19
0	0	10	3.24	3.19	.13	2	4	4	1.65	1.42	.20
0	0	12	1.80	1.59	.17	2	4	6	9.52	9.62	.20
0	2	2	1.85	1.58	.12	*2	4	8	0.44	0.20	.44
*2	2	4	0.33	0.24	.33	2	4	10	4.62	4.46	.13
0	2	6	10.38	10.34	.20	*2	6	6	0.44	0.51	.44
0	2	8	3.31	-3.26	.13	2	6	8	3.82	4.15	.13
2	2	10	5.35	5.39	.14	*2	6	10	1.04	0.84	.33
*2	2	12	0.48	-0.60	.48	*2	0	8	0.48	-0.28	.48
*0	4	4	14.33	14.10	.24	*3	3	3	0.40	-0.49	.40
*0	4	6	0.40	-0.38	.40	*3	3	5	2.96	-3.19	.12
0	4	8	5.33	5.31	.13	*3	3	7	0.44	-0.62	.44
0	4	10	1.52	1.47	.20	3	3	9	1.27	1.44	.27
0	6	6	7.82	7.74	.19	*3	3	11	0.48	0.46	.48
*0	6	8	0.48	-0.32	.40	3	5	5	1.24	0.96	.27
0	6	10	3.57	3.56	.12	*3	5	7	0.44	-0.41	.44
0	8	8	2.02	1.98	.17	3	5	9	1.25	1.29	.27
1	1	1	7.38	7.18	.13	3	5	11	0.48	0.47	.48
*1	1	3	0.33	-0.22	.33	*3	7	7	0.48	-0.18	.48
1	1	5	4.25	4.16	.12	3	7	9	1.29	1.38	.25
*1	1	7	0.40	-0.31	.40	4	4	4	12.63	13.05	.22
1	1	9	2.93	2.75	.14	*4	4	6	0.44	0.67	.44
1	1	11	0.95	1.01	.32	4	4	8	5.38	5.24	.15
1	3	3	5.19	-5.23	.11	*4	4	10	0.48	0.68	.48
1	3	5	1.33	1.27	.20	4	6	6	5.16	5.10	.12
1	3	7	2.85	-2.92	.14	4	6	8	0.48	0.65	.48
1	3	9	1.07	1.73	.20	*4	6	10	2.53	2.48	.16
*1	3	11	0.40	0.19	.40	4	8	8	2.68	2.81	.14
*1	5	5	0.40	0.59	.40	5	5	5	2.16	-1.90	.16
*1	5	7	0.44	0.74	.44	*5	5	7	0.48	-0.29	.48
1	5	9	1.75	1.77	.20	5	5	9	1.17	1.21	.27
*1	5	11	0.48	0.47	.48	*5	7	7	1.86	1.92	.20
*1	7	7	0.44	-0.46	.44	6	6	6	1.22	1.16	.28
*1	7	9	0.48	0.47	.48	6	6	8	2.83	3.03	.15
2	2	2	5.85	-5.20	.13	*7	7	7	0.48	0.50	.48

The reorienting (NH₄)[II] ion is probably involved in hydrogen bonding as the N(2)–F(2) and N(2)–F(1) distances are 2·67 (1) and 3·07 (1) Å, with N(2)–H$_{xyz}$...F(2) and N(2)–H$_{xzz}$...F(1) angles of 173 and 169°. The N(2)–H$_{xyz}$ and N(2)–H$_{xzz}$ distances are 0·97 and 1·12 Å.

In (NH₄)₂SiF₆, which is cubic with space group $Fm3m$, the NH₄⁺ ion at (¼,¼,¼) is similarly disordered (Schlemper, Hamilton & Rush, 1966). These authors placed partial hydrogen atoms H$_{xzz}$ in positions 96(k) to account for the triangular shape of the hydrogen peak, which gave an N–F distance of 2·996 (2) Å, and N–H$_{xzz}$...F angle of 155·0 (8)°.

Conclusion

(NH₄)₃ZrF₇ is a complex example of a dynamically disordered crystal. The ZrF₇³⁻ ion and the two crystallographically different NH₄⁺ ions are all involved in the disorder, which is probably influenced by hydrogen bonding forces.

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