The Crystal Structure of Ammonium Beryllium Fluoride, $(NH_4)_2BeF_4$.

By

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(With one figure.)

The orthorhombic crystal, $(NH_4)_2BeF_4$, has been investigated by the use of complete rotation and oscillation photographs. It is found that $a_0 = 5.8$ Å, $b_0 = 10.2$ Å, and $c_0 = 7.5$ Å. The atomic arrangement is that of K_2SO_4, which structure is also assumed by $(NH_4)_2SO_4$. This shows that the BeF_4^{2-} group has much the same size and shape as the SO_4^{2-} group, which is to be expected from consideration of ionic sizes.

Crystallographic investigations of ammonium beryllium fluoride $(NH_4)_2BeF_4$, have shown that it is orthorhombic bipyramidal with axial ratios $a : b : c = 0.5688 : 1 : 0.7367$[2]). It is isomorphous with K_2BeF_4, but not with Na_2BeF_4.

Well formed crystals of it were made available to me through the kindness of Mr. Charles F. Hill, of this laboratory, who had prepared them in the course of another investigation. The crystals consisted of plates flattened along the c axis and longer along the a axis than along the b. Prominent faces were (001), (010), and (110).

The Unit of Structure and Space-group Symmetry.

Complete rotation photographs were made about all three axes with *Mo* radiation filtered through zirconia and the size of the unit cell was found to be

$$a_0 = 5.8\ \text{Å} \qquad b_0 = 10.2\ \text{Å} \qquad c_0 = 7.5\ \text{Å}$$

to an accuracy of about 0.1 Å. This agrees well with the axial ratios listed by Groth. If the unit cell contains four molecules, the calculated density is 1.80 g/cm³. This value was roughly verified by weighing a

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[1]) National Research Fellow.

[2]) Groth, Chemische Krystallographie, **1**, 342.

crystal and computing its volume from micrometer measurements of its dimensions.

Eight oscillation photographs were taken about (010) and two about (100) in such a way that all planes would have the opportunity to reflect. The angle of oscillation was 16° in each case. Reflections were absent from planes $(h\,k\,0)$ with $h + k$ odd, and from $(h\,0\,l)$ where l was odd. Since the crystallographic symmetry is holohedral, all space groups are eliminated except V_h^1, V_h^5, V_h^{13}, and V_h^{16}. The last is the only one which requires both extinctions and is much the most probable. The space group is thus determined to be:

$$V_h^{16} - P\,m\,c\,n.$$

The Atomic Arrangement.

The following possible positions are provided by this space group:

(a)	$0\,0\,0;$	$\frac{1}{2}\,0\,0;$	$\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2};$	$0\,\frac{1}{2}\,\frac{1}{2}$
(b)	$0\,\frac{1}{2}\,0;$	$\frac{1}{2}\,\frac{1}{2}\,0;$	$\frac{1}{2}\,0\,\frac{1}{2};$	$0\,0\,\frac{1}{2}$
(c)	$\frac{1}{4}\,u\,v;$	$\frac{1}{4}, \frac{1}{2} - u, \frac{1}{2} + v,$	$\frac{3}{4}, \frac{1}{2} + \mu, \frac{1}{2} - v;$	$\frac{3}{4}\,\bar{u}\,\bar{v}$
(d)	$x\,y\,z;$	$\frac{1}{2} - x, y, z;$	$x, \frac{1}{2} - y, \frac{1}{2} + z;$	$\frac{1}{2} + x, \frac{1}{2} + y, \frac{1}{2} - z;$
	$\bar{x}\,\bar{y}\,\bar{z};$	$\frac{1}{2} + x, \bar{y}, \bar{z};$	$\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z;$	$\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z.$

The origin of coordinates is here taken at a center of symmetry. Positions (a) and (b) are at centers of symmetry, (c) is on a plane of symmetry, while (d) is the general position. If the Be^{2+} ions are surrounded by four F^- ions at the corners of a regular tetrahedron, as seems almost certain, they cannot lie at a center of symmetry, but must lie at (c), on the plane of symmetry. Furthermore, in the BeF_4^{2-} group, two of the F^- ions must lie on the plane in positions (c) and the other two off the plane at (d). The NH_4^+ ions can be shown to lie on the plane from intensity considerations.

Thus it is observed that (200) is slightly stronger than (400), while (600) weakly reflects. If we assume the reasonable value of 1.61 Å for the $Be—F$ distance and place the F^- ions at the corners of a regular tetrahedron, then all the x coordinates are fixed except those of NH_4^+. If these are placed in positions (d), it is found that the calculated intensity from (400) is much greater than (200) except near $x = \frac{1}{4}$. But an atom cannot lie nearer to a plane of symmetry than its own radius, so the position (d) is excluded. The results of calculations for the other positions are shown in Table I.

Table I. Calculated Intensity.

	Both NH_4^+ at (a) or (b)	One NH_4^+ at (a) or (b); one at (c)	Both NH_4^+ at (c)	Observed Intensity
I_{200}	128	57	2060	6
I_{400}	2570	2570	2570	5
I_{600}	0	13	50	1

From Table I it is evident that the NH_4^+ ions lie in two sets of positions (*c*). The small disagreement of calculated and observed intensities is probably due to the temperature factor, which was not considered. For the scattering factor of NH_4^+, the values assumed by Pauling[1] were chosen. He assumed $f_{NH_4^+} = f_N + f_{O^-} - f_O$. It was later found that unpublished experimental values of Dr. G. A. Morton check these assumed values fairly closely except for small values of $\sin \theta/\lambda$, so no great error is to be anticipated here.

The atomic positions have thus been found to be:

NH_4 (1)	at $\frac{1}{4}\,u\,v;\ \frac{1}{4}, \frac{1}{2}-u, \frac{1}{2}+v;\ \frac{3}{4}, \frac{1}{2}+u, \frac{1}{2}-v;\ \frac{3}{4}\,\bar{u}\,\bar{v}$
NH_4 (2)	at $\frac{1}{4}\,u'\,v'$; etc.
Be	at $\frac{1}{4}\,u''\,v''$; etc.
F (1)	at $\frac{1}{4}\,u_1\,v_1$; etc.
F (2)	at $\frac{1}{2}\,u_2\,v_2$; etc.
F (3)	at $x\,y\,z;\ \frac{1}{2}-x, y, z;\ x, \frac{1}{2}-y, \frac{1}{2}+z;\ \frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}-z;$ $\bar{x}\,\bar{y}\,\bar{z};\ \frac{1}{2}+x, \bar{y}, \bar{z};\ \bar{x}, \frac{1}{2}+y, \frac{1}{2}-z; \frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z.$

Rigorous determination of the atomic coordinates cannot be made because of the large number of parameters involved. However, it is noticed that all the atomic positions agree with those of K_2SO_4, which structure is also assumed by $(NH_4)_2SO_4$. The lengths of the axes are also nearly the same. In $(NH_4)_2SO_4$, $a_0 = 5.95$, $b_0 = 10.5$, $c_0 = 7.73$ Å. It might be expected that $(NH_4)_2BeF_4$ would assume this structure since the BeF_4^{2-} group ought to be about the same size and shape as the SO_4^{2-} group. Also each is isomorphous with its corresponding potassium salt and different from its sodium salt.

It was found that this structure does indeed give reasonably good agreement between calculated and observed intensities when the parameters are varied somewhat. Values of parameters yielding best agreement are given in Table II. along with those of $(NH_4)_2SO_4$ for comparison. The agreement between calculated and observed intensities is shown in

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[1] Z. Krist. 85, 380. 1933.

Table III. It was felt that this agreement could be improved by further variation of the parameters, as the intensities are quite sensitive, but such changes in the parameters would be small and it was not thought worth while.

Table II. Parameters of Structure.

Substance	NH_4 (1)		NH_4 (2)		Be		F (1)		F (2)		F (3)		
	u	v	u'	v'	u''	v''	u_1	v_1	u_2	v_2	x	y	z
$(NH_4)_2BeF_4$	.393	.675	—.325	—.046	.417	.263	.390	.051	.573	.300	.024	.353	.350
$(NH_4)_2SO_4$	.417	.685	—.311	0	.417	.250	.417	.056	.549	.315	.045	.351	.315

Table III. X-Ray Data.

Photograph No.	hkl	Calc. Int.	Obs. Int.	Photograph No.	hkl	Calc. Int.	Obs. Int.
1	011	45	0	5	202	80	3
	021	496	9		212	2234	7
	002	299	8		222	299	5
	012	0	0				
	022	336	8	6	111	448	6
	104	93	3		121	1	0
	114	22	2		202	80	3
	124	102	2		212	2234	7
					222	299	5
2	002	299	7		211	578	5
	012	0	0		221	1563	8
	022	336	6		311	12	0
	013	3329	9		321	83	2
	023	1277	5				
	004	76	3	7	211	578	2
	014	272	6		221	1563	8
	104	93	2		302	128	1
	114	22	1		312	0	0
	124	102	1		322	1	0
3	102	5	0	8	110	110	2
	112	23	3		130	561	9
	122	18	2		200	1815	6
					220	487	3
4	102	5	0		310	77	1
	112	23	3		400	1774	5
	122	18	1				
	104	93	2				
	114	17	1				
	124	102	2				

The structure is shown in the diagram. Each Be^{2+} is surrounded by four F^- at the corners of a regular tetrahedron at a distance of 1.61 Å. Half of the NH_4^+ ions are surrounded as follows: $3F^-$ at 2.81 Å, $2F^-$ at 2.92 Å, $3F^-$ at 3.04 Å. The other half have $1F^-$ at 2.79 Å, $3F^-$ at 2.82 Å, and $5F^-$ at 2.98 Å. There is no particular indication of hydrogen bonds between N and F, such as Pauling[1]) found for NH_4F, but the data are not sufficiently accurate to exclude them. The interionic distances agree with what should be expected.

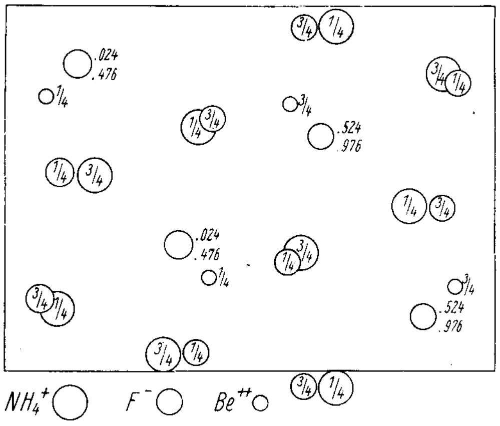

Fig. 1. Structure of $(NH_4)_2BeF_4$.

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1) loc. cit.

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