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THE CRYSTAL STRUCTURES OF AMMONIUM FLUOFERRATE, FLUO-ALUMINATE AND OXYFLUOMOLYBDATE

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Introduction

Crystals of ammonium fluo-aluminate $(\text{NH}_4)_3\text{AlF}$, fluotitanate $(\text{NH}_4)_3\text{-TiF}_6$, fluovanadate $(\text{NH}_4)_3\text{VF}_6$, fluochromate $(\text{NH}_4)_3\text{CrF}_6$ and fluoferrate $(\text{NH}_4)_3\text{FeF}_6$, are described by Groth¹ as apparently isomorphous, optically isotropic octahedra. Ammonium oxyfluomolybdate $(\text{NH}_4)_3\text{-MoO}_3\text{F}_3$ and oxyfluotungstate $(\text{NH}_4)_3\text{WO}_3\text{F}_3$, are also described² as forming similar small isotropic octahedra. The structures of ammonium chloroplatinate³ $(\text{NH}_4)_2\text{PtCl}_6$, chlorostannate⁴ $(\text{NH}_4)_2\text{SnCl}_6$ and fluosilicate⁵ $(\text{NH}_4)_2\text{SiF}_6$, have been determined; it seemed of interest to investigate these complex fluorides for the purpose of finding, if possible, the changes in structure produced by the introduction of a third ammonium group. Moreover, the effect of replacing three of the six halogen atoms by oxygen could not be confidently predicted and it was thought that a study of these oxyfluorides also was desirable.

Crystals of ammonium fluoferrate were obtained by the slow evaporation of a solution of ammonium fluoride and ferric chloride. The light yellow crystals, less than 0.8 mm. on an edge, were found on analysis to contain only ammonia, iron and fluorine. Transparent plates of ammonium fluo-aluminate as large as 4 or 5 mm. on an edge were obtained similarly from a solution of ammonium fluoride and aluminum chloride and were also found to be free from impurities. Brilliant white crystals of ammonium oxyfluomolybdate about 1 mm. in diameter resulted from the slow evaporation of a solution of molybdic acid, ammonium hydroxide and ammonium fluoride. The crystals of all three substances were observed to be optically isotropic and to show the form $\{111\}$; subsidiary faces of $\{100\}$ were in some cases developed by ammonium fluo-aluminate.

Spectral, Laue and powder photographs were used in this investigation, the data so obtained being interpreted with the aid of the theory of space groups.⁶ Spectral photographs of the K-radiation of molybdenum were made either by reflection from a developed face of the ro-

¹ Groth, "Chemische Krystallographie," Engelmann, Leipzig, 1906, vol. 1, p. 416.

² Ref. 1, p. 586.

³ Wyckoff and Posnjak, THIS JOURNAL, 43, 2292 (1921).

⁴ Dickinson, *ibid.*, 44, 276 (1922).

⁵ Bozorth, *ibid.*, 44, 1066 (1922).

⁶ See Refs. 3 and 4 for a more detailed description of the methods used.

tating crystal or, for small specimens, by reflection during the transmission of the beam through the crystal. Laue photographs were made with a tube with a tungsten anticathode operated at a peak voltage of 52,000 v., so that the minimum wave length of X-rays incident on the crystal was about 0.24 Å. The planes producing the Laue spots were identified with the aid of gnomonic projections. Powder photographs were made with an apparatus similar to that described by Davey,⁷ using a molybdenum tube and having a zirconia filter directly in front of the film.

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The Structure of Ammonium Fluoferrate

In Table I are given data for ammonium fluoferrate leading to the value 4.55 Å. for d_{100}/n . It was found that in order to account for the

TABLE I
SPECTRAL DATA FROM (100) OF $(\text{NH}_4)_3\text{FeF}_6$

Order of reflection	Line ^a	Angle of reflection	d_{100}/n Å.	Estimated intensity ^b
<i>n</i>	β	3° 59.3'	4.53	m
<i>n</i>	α	4 28	4.56	s
2 <i>n</i>	β	7 58	4.55	m
2 <i>n</i>	α	8 57.7	4.56	s
3 <i>n</i>	β	11 59	4.56	vw
3 <i>n</i>	α	13 32.7	4.55	mw

^a The symbol β denotes in this and subsequent tables the line $\text{MoK}\beta$ (0.6311 Å.); the symbol α , the line $\text{MoK}\alpha$ (0.710 Å.).

^b Abbreviations used for all spectral intensities in this paper are: vs, very strong; s, strong; ms, medium strong; m, medium; mw, medium weak; w, weak; vw, very weak; a, absent.

production of the observed Laue reflections shown in Table II by means of X-rays present in the incident beam it would be necessary to place $n = 2$. No reflections remained unaccounted for by such a unit with $d_{100} = 9.10$ Å., which may accordingly be accepted as the correct one. This unit contains 4 $(\text{NH}_4)_3\text{FeF}_6$, corresponding to a calculated density of 1.96 g./cc. The density of a sample of precipitated ammonium fluoferrate obtained by pouring together solutions of ammonium fluoride and ferric chloride was found by means of a pycnometer with benzene to be 1.91. A powder photograph of this sample showed weak lines of ammonium chloride, the presence of which explains the slight disagreement in the densities. The value 9.10 Å. for d_{100} was verified by the powder photographic data, which are not given because they did not aid in determining the structure.

⁷ Davey, *J. Optical Soc. Am.*, 5, 479 (1921).

TABLE II
LAUE PHOTOGRAPHIC DATA FROM $(\text{NH}_4)_2\text{FeF}_6$

	hkl	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity	S for $\mu = 0.21$
Photograph No. 2, through (110)	104	2×1.10	2×0.45	0.3	0.76
	$\bar{5}71$	1.05	.44	.4	1.28
Photograph No. 3, through (110)	$01\bar{4}$	2×1.10	$2 \times .39$.05	0.76
	$3\bar{2}\bar{2}$	2×1.10	$2 \times .39$.15	2.07
Photograph No. 4, through (111)	$\bar{5}1\bar{7}$	1.05	.44	.3	1.28
	$\bar{7}35$	1.00	.44	.25	0.34
	$\bar{7}17$	0.91	.39	.15	0.66
	$\bar{3}40$	$2 \times .91$	$2 \times .38$.20	1.57
	$\bar{1}59$.88	.44	.25	3.03
	$93\bar{5}$.85	.39	.15	2.09
	432	$2 \times .84$	$2 \times .42$.10	1.10
	$\bar{2}5\bar{1}$	$2 \times .83$	$2 \times .42$.20	3.08
	$5\bar{7}7$.82	.41	.08	0.04
	$\bar{7}91$.80	.40	.04	1.10
	$\bar{4}14$	$2 \times .79$	$2 \times .41$.06	0.67
	$43\bar{3}$	$2 \times .78$	$2 \times .41$.10	2.06
	$0\bar{3}\bar{5}$	$2 \times .78$	$2 \times .41$.15	4.36

No Laue spots correspond to first-order reflections except those from planes with all indices odd; this indicates that the arrangement of the atoms (with the possible exception of those of hydrogen) is based on a face-centered lattice. The coordinates of the positions of 12 N, 4 Fe, and 24 F for the only arrangements fulfilling these conditions are⁸ as follows.

From space groups T_h^3 , O^3 , or O_h^5

4 Fe or 4 N at 4(b): $000; \frac{1}{2}\frac{1}{2}0; \frac{1}{2}0\frac{1}{2}; 0\frac{1}{2}\frac{1}{2}$

4 N or 4 Fe at 4(c): $\frac{1}{2}\frac{1}{2}\frac{1}{2}; \frac{1}{2}00; 0\frac{1}{2}0; 00\frac{1}{2}$

8 N at 8(e): $\frac{1}{4}\frac{1}{4}\frac{1}{4}; \frac{1}{4}\frac{3}{4}\frac{3}{4}; \frac{3}{4}\frac{1}{4}\frac{3}{4}; \frac{3}{4}\frac{3}{4}\frac{1}{4}; \frac{3}{4}\frac{3}{4}\frac{3}{4}; \frac{3}{4}\frac{1}{4}\frac{1}{4}; \frac{1}{4}\frac{1}{4}\frac{3}{4}; \frac{1}{4}\frac{3}{4}\frac{1}{4}$

24 F at 24(a): $u00; u + \frac{1}{2}\frac{1}{2}0; u + \frac{1}{2}0\frac{1}{2}; u\frac{1}{2}\frac{1}{2}; \bar{u}00; \frac{1}{2} - u\frac{1}{2}0; \frac{1}{2} - u0\frac{1}{2}; \bar{u}\frac{1}{2}\frac{1}{2};$

$0u0; \frac{1}{2}u + \frac{1}{2}0; \frac{1}{2}u\frac{1}{2}; 0u + \frac{1}{2}\frac{1}{2}; 0\bar{u}0; \frac{1}{2}\frac{1}{2} - u0; \frac{1}{2}\bar{u}\frac{1}{2}; 0\frac{1}{2} - u\frac{1}{2};$

$00u; \frac{1}{2}\frac{1}{2}u; \frac{1}{2}0u + \frac{1}{2}; 0\frac{1}{2}u + \frac{1}{2}; 00\bar{u}; \frac{1}{2}\frac{1}{2}\bar{u}; \frac{1}{2}0\frac{1}{2} - u; 0\frac{1}{2}\frac{1}{2} - u$

or at 24(c): $\frac{1}{4}\frac{1}{4}0; \frac{1}{4}\frac{3}{4}0; \frac{3}{4}\frac{1}{4}0; \frac{3}{4}\frac{3}{4}0; 0\frac{1}{4}\frac{1}{4}; 0\frac{1}{4}\frac{3}{4}; 0\frac{3}{4}\frac{1}{4}; 0\frac{3}{4}\frac{3}{4}; \frac{1}{4}0\frac{1}{4}; \frac{1}{4}0\frac{3}{4}; \frac{3}{4}0\frac{1}{4}; \frac{3}{4}0\frac{3}{4}; \frac{1}{4}\frac{1}{4}\frac{1}{4}; \frac{1}{4}\frac{1}{4}\frac{3}{4};$

$\frac{1}{4}\frac{3}{4}\frac{1}{4}; \frac{1}{4}\frac{3}{4}\frac{3}{4}; \frac{3}{4}\frac{1}{4}\frac{1}{4}; \frac{3}{4}\frac{1}{4}\frac{3}{4}; \frac{3}{4}\frac{3}{4}\frac{1}{4}; \frac{3}{4}\frac{3}{4}\frac{3}{4}; \frac{1}{4}\frac{1}{4}\frac{1}{4}; \frac{1}{4}\frac{1}{4}\frac{3}{4}$

From space-groups T^2 or T_d^2

4 N or 4 Fe at 4(b)

4 N or 4 Fe at 4(c)

4 N or 4 Fe at 4(d): $\frac{1}{4}\frac{1}{4}\frac{1}{4}; \frac{1}{4}\frac{3}{4}\frac{3}{4}; \frac{3}{4}\frac{1}{4}\frac{3}{4}; \frac{3}{4}\frac{3}{4}\frac{1}{4}$

4 N or 4 Fe at 4(e): $\frac{3}{4}\frac{3}{4}\frac{3}{4}; \frac{3}{4}\frac{1}{4}\frac{1}{4}; \frac{1}{4}\frac{1}{4}\frac{3}{4}; \frac{1}{4}\frac{3}{4}\frac{1}{4}$

24 F at 24(a) or at 24(b): $\frac{1}{4}\frac{1}{4}u; \bar{u}\frac{3}{4}\frac{3}{4}; u + \frac{1}{2}\frac{3}{4}\frac{3}{4}; \frac{3}{4}\frac{1}{2} - u\frac{3}{4}; \frac{1}{4}\frac{1}{4}\bar{u}; u\frac{3}{4}\frac{3}{4}; \frac{1}{2} - u\frac{3}{4}\frac{3}{4};$

$\frac{1}{4}u + \frac{1}{2}\frac{3}{4}; \frac{3}{4}\frac{1}{2}\bar{u}; \frac{1}{4}u\frac{1}{2}; \frac{1}{2} - u\frac{1}{2}\frac{3}{4}; \frac{3}{4}\frac{1}{2}u + \frac{1}{2}; \frac{3}{4}\frac{3}{4}u; \frac{3}{4}\bar{u}\frac{1}{2};$

$u + \frac{1}{2}\frac{1}{4}\frac{3}{4}; \frac{3}{4}\frac{3}{4}\frac{1}{2} - u; u\frac{1}{4}\frac{1}{4}; \frac{1}{2}\bar{u}\frac{3}{4}; \frac{3}{4}u + \frac{1}{2}\frac{1}{4}; \frac{1}{4}\frac{1}{4}\frac{1}{2} - u;$

$\bar{u}\frac{1}{4}\frac{3}{4}; \frac{3}{4}u\frac{3}{4}; \frac{1}{2}\frac{1}{2} - u\frac{1}{2}; \frac{1}{4}\frac{3}{4}u + \frac{1}{2}$

⁸ Wyckoff, "The Analytical Expression of the Results of the Theory of Space-Groups," *Carnegie Inst. Pub.*, No. 318 (1922).

It will be noticed that no arrangement is possible in which all of the nitrogen atoms are in equivalent positions.

Any arrangement with the fluorine atoms at 24(c) will give the same structure factor to all first-order reflections from planes with all indices odd. The observation that, for example, {951} reflects more strongly than {771} at the same wave length despite its smaller interplanar distance accordingly eliminates this. The arrangement with Fe at 4(d), N at 4(b), 4(c), and 4(e), and F at 24(a) places six fluorine atoms at octahedron corners around an atom of nitrogen rather than one of iron. The chemical improbability of this structure provides considerable reason for not giving it further consideration; however, it was found possible to eliminate it definitely by means of X-ray data. It can be shown that, if this be the structure of the substance, the spectral data from (111) require that the parameter u should lie in the region between 0.20 and 0.30. Throughout this region the structure factor for {410} ($n = 2$) is greater than that for {322} ($n = 2$), except at $u = 0.25$, where they are equal. The experimental observation that {322} reflects much more strongly than {410} accordingly makes this structure impossible. The only remaining distinct arrangement can be derived from space groups T^2 or T_d^2 by placing Fe at 4(b), N at 4(c), 4(d), and 4(e), and F at 24(a), or from T_h^3 , O^3 , or O_h^3 by placing N at 8(e) instead of at 4(d) and 4(e).

Planes giving useful Laue reflections can be divided into three classes. These are, with corresponding values of the structure factor S , the following.

Class 1; all indices odd: $n = 1, S = 4\bar{F}e - 4\bar{N} + 8\bar{F}(\cos 2\pi uh + \cos 2\pi uk + \cos 2\pi ul)$

Class 2; two indices odd, one even: $n = 1, S = 0; n = 2, S = 4\bar{F}e + 12\bar{N} + 8\bar{F}(\cos 4\pi uh + \cos 4\pi uk + \cos 4\pi ul)$

Class 3; one index odd, two even: $n = 1, S = 0; n = 2, S = 4\bar{F}e - 4\bar{N} + 8\bar{F}(\cos 4\pi uh + \cos 4\pi uk + \cos 4\pi ul)$

Comparison may be made, it will be seen, between planes in each class and between those of Classes 1 and 3 ($n = 2$) with only qualitative assumptions regarding relative reflecting powers; care must be used with planes with small values of S .

A spectral photograph from (111) showed five orders of reflection, with intensities strong, medium, weak, medium and weak. This shows that the structure factor is greater for $n = 4$ than for $n = 2$, and greater for $n = 5$ than for $n = 3$. Curves of these structure factors are shown in Fig. 1 for $u = 0$ to $u = 0.50$, which includes all distinct structures. In their calculation relative reflecting powers of different atoms have been assumed proportional to their atomic numbers; however, a considerable deviation from this would not invalidate the arguments given here. It will be seen that these spectral intensities limit u to the region between

about 0.16 and 0.25. Similarly calculated curves of the structure-factors of some useful planes reflecting on Laue photographs for a range of values

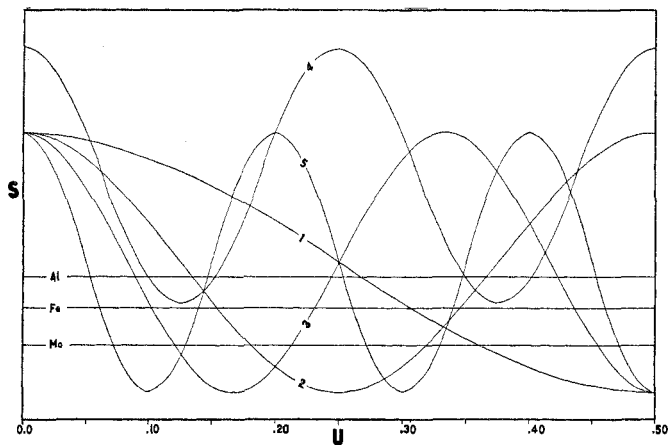


Fig. 1.—Structure-factor curves for (111). The order of reflection is given by the numbers on the curves. Positive values of S are to be read both above and below the horizontal lines, which have the value $S=0$ for the substances indicated.

of u are given in Fig. 2. It was observed that {751} gave a stronger reflection than {410} ($n = 2$), requiring u to be less than 0.217, and that

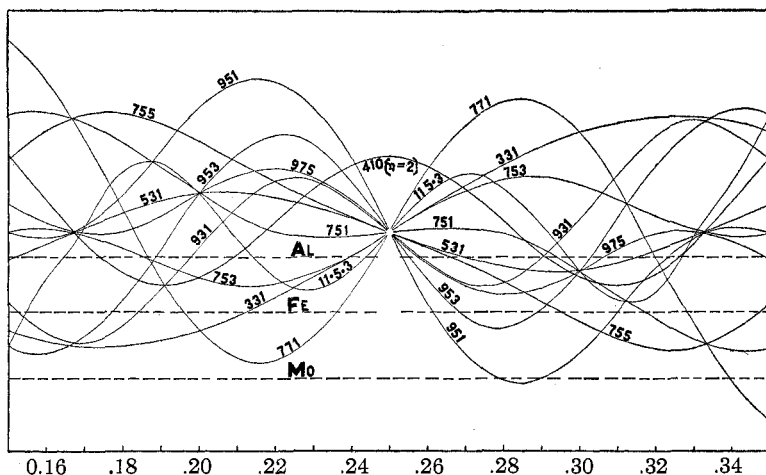


Fig. 2.—Structure-factor curves for the planes with the indices shown. Positive values of S are to be read both above and below the horizontal lines, which have the value $S=0$ for the substances indicated.

{953}, with considerably smaller interplanar distance, gave as strong a reflection as {771}, requiring u to be greater than 0.187. Further definite

limitation of possible values of u was not accomplished; values of S for $u = 0.21$, which seems to be the most probable value, are given in Table II for comparison with the observed Laue intensities; the agreement is good, except for a few planes for which S would be considerably affected by a small change in the relative reflecting powers of different atoms.

Chemical evidence strongly indicates that each nitrogen atom is surrounded by 4 hydrogen atoms. Space groups T^2 and T_d^2 provide the only way in which this can be accomplished. By assigning different values to the parameter v in 16(a), with coördinates,

$$\begin{aligned} &v\bar{v}\bar{v}; v + \frac{1}{2}v + \frac{1}{2}v; v + \frac{1}{2}v\bar{v} + \frac{1}{2}; v\bar{v} + \frac{1}{2}v + \frac{1}{2}; v\bar{v}\bar{v}; v + \frac{1}{2}\frac{1}{2} - v\bar{v}; \\ &v + \frac{1}{2}\bar{v}\frac{1}{2} - v; v\frac{1}{2} - v\frac{1}{2} - v; \bar{v}\bar{v}\bar{v}; \frac{1}{2} - v\bar{v} + \frac{1}{2}\bar{v}; \frac{1}{2} - v\bar{v}\frac{1}{2} - v; \bar{v}\bar{v} + \frac{1}{2}\frac{1}{2} - v; \\ &\bar{v}\bar{v}\bar{v}; \frac{1}{2} - v\frac{1}{2} - v\bar{v}; \frac{1}{2} - v\bar{v}\bar{v} + \frac{1}{2}; \bar{v}\frac{1}{2} - v\bar{v} + \frac{1}{2} \end{aligned}$$

the 48 hydrogen atoms can be placed in such a way that each nitrogen atom is surrounded tetrahedrally by 4 hydrogen atoms. A probable arrangement of the hydrogen atoms results on giving v values of $\frac{1}{4} - d$, $\frac{1}{2} - d$, and $\frac{3}{4} + d$, in which d is the hydrogen-to-nitrogen distance; these positions are indicated by the corners of the tetrahedra in Fig. 4.

The Structure of Ammonium Fluo-aluminate

Spectral data for ammonium fluo-aluminate, given in Table III, show d_{111}/n to be 4.85 Å. If n were 1, the unit of structure would have $d_{100} = 8.40$ Å., and would contain $4(\text{NH}_4)_3\text{AlF}_6$. The calculated density 2.17 g./cc. is somewhat greater than 2.02, the value determined by a suspension method on small crystals, which showed considerable variation among themselves.

TABLE III
SPECTRAL DATA FROM (111) OF $(\text{NH}_4)_3\text{AlF}_6$

Order of reflection	Line	Angle of reflection	d_{111}/n Å.	Estimated intensity
n	β	3° 43.6'	4.856	ms
n	α	4 11.5	4.861	vs
$2n$	β	7 29	4.845	ms
$2n$	α	8 25.5	4.847	vs
$3n$	β	11 15.3	4.846	vw
$3n$	α	12 40.6	4.851	mw
$4n$	β	15 6.5	4.844	vw
$4n$	α	17 0	4.855	mw

Values of $n\lambda$ as low as 0.095 Å., taking $d_{100} = 8.40$, were calculated for Laue reflections, indicating a unit with $d_{100} = 25.20$ Å., containing 256 molecules. However, there are the following reasons, other than the probable isomorphism with ammonium fluoferrate, for believing that this indication is illusory, namely, that the true unit has $d_{100} = 8.40$ Å., and that the Laue photographs were taken with crystals twinned on (111). (1) In Fig. 3 are plotted curves showing the relative intensities of {531} and

{13.11.5} ({531} on the twin) on two Laue photographs taken with crystals prepared at different times. It will be seen that there is pronounced disagreement, definitely indicating twinning. (2) All of the 20 lines observed on a powder photograph of the substance (Table IV) are accounted for by the small unit; these photographs are not influenced by twinning. The absence of any reflections requiring a larger unit makes it improbable that such a unit exists. (3) Only a few very complicated forms such as {25.17.7} gave low values of $n\lambda$. If indices ($h'k'l'$) based on the axes of the twin are calculated by means of the equations⁹ $h' = 2l + 2k - h$, $k' = 2h + 2l - k$, and $l' = 2h + 2k - l$, no reflections remain unexplained by the small unit. Moreover, the ratio of intensities

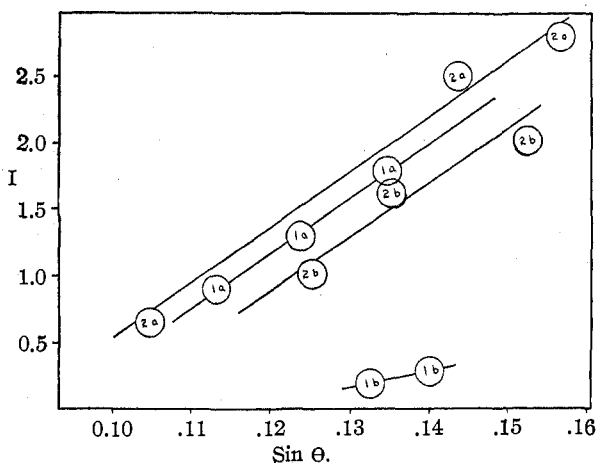


Fig. 3.—Relative intensities of reflection of 531; 1a and 1b are for the two individuals composing one twinned crystal of $(\text{NH}_4)_3\text{AlF}_6$ and 2a and 2b for another twinned crystal.

from the two individuals composing the twinned crystal whenever it can be determined is found to be about 8:1 for one crystal and 8:6 for the other.

These indications were accepted as showing the unit of structure to be the small one with $4(\text{NH}_4)_3\text{AlF}_6$. It was found that some Laue spots were produced by the simultaneous reflection from one plane in one individual of the twinned crystal and from another in the other. In many cases, however, no reflection could occur from one of the two planes because wave lengths shorter than 0.24 Å. would have been required. These planes, free from ambiguity, could be compared with each other in the usual way. Only planes with all indices odd gave first-order reflections. Abnormal intensity relations occurred, eliminating any struc-

⁹ Tutton, "Crystallography," Macmillan and Co., London, 1911, p. 340.

TABLE IV
POWDER PHOTOGRAPHIC DATA FROM $(\text{NH}_4)_2\text{AlF}_6$; $d_{100} = 8.40 \text{ \AA}$.

hkl^a	d_{hkl} calculated Å.	d_{hkl} observed Å.	Estimated intensity	Number of cooperating planes	S for $u = 0.197$
111	4.85	4.9	6	8	1.32
200	4.20	4.20	4	6	1.55
220	2.969	2.96	3	12	1.31
311	2.535	2.53	1.5	24	0.15
222	2.423	2.42	5	8	2.03
400	2.100	2.10	6	6	4.13
331	1.928	1.93	0.1	24	1.02
420	1.879	1.875	.2	24	0.78
422	1.717	1.720	.05	24	.55
333, 511	1.619	1.616	5	8, 24	2.19, 1.98
440	1.485	1.481	3	12	3.36
531	1.420	1.421	2	48	0.82
442, 600	1.400	24, 6	.02, 2.75
620	1.329	1.326	1	24	2.52
533	1.281	24	0.35
622	1.269	1.269	0.05	24	.82
444	1.213	1.210	0.1	8	2.60
711, 551	1.189	1.175	2	24, 24	0.26, 2.65
640	1.166	1.161	0.2-0.4	24	1.99
642	1.123	1.120	1	48	1.75
731, 553	1.093	1.094	1	48, 24	0.91, 1.49
800	1.050	6	3.00
733	1.028	24	2.08
820, 644	1.020	24, 24	0.34, 1.22
822, 660	0.991	0.985	0.2	24, 12	.58, 3.72
555, 751	.970	0.970	0.5	8, 48	3.32, 0.93
662	.964	24	0.37
840	.940	.940	0.2	24	2.24
911, 753	.922	24, 48	1.13, 0.24
842	.916	48	1.11
664	.895	.894	0.2	24	2.96

^a In this table the second order of (211) is written (422), and similarly for all orders.

ture with F at 24(c); the second improbable arrangement was not eliminated by X-ray data on account of the similarity in reflecting powers of Al and N.

The value of u in the remaining arrangement can be closely limited. The spectral data show the structure-factor for $n = 2$ from (111) to be greater than for $n = 1$ and for $n = 4$ greater than for $n = 3$. The parameter u is accordingly limited to the region between 0.16 and 0.30 and that between 0.42 and 0.50. The latter can be eliminated by means of Laue data. Laue data from the two crystals for which the intensity ratios of twins are about 8:1 and 8:6 are given in Table V. Among the unambiguous intensity relations are these: $\{953\} \gg \{753\}$, requiring u to be between 0.188 and 0.25; and $\{11.5.3\} > \{975\}$, requiring u to

be less than 0.200. It will be observed that {531} reflected much more strongly than {331}, indicating the true position of the line $S = 0$ to be somewhat lower than drawn in Fig. 2 (corresponding to a greater reflecting power for Al). With this knowledge, the relation {931} > {753} places u above 0.194. The most probable value for u is 0.197; the complete agreement of this structure with the experimental data can be seen by reference to Tables IV and V. It is necessary to mention that

TABLE V
LAUE PHOTOGRAPHIC DATA FROM $(\text{NH}_4)_3\text{AlF}_6$, THROUGH (111)
CRYSTAL NO. 1; INTENSITY RATIO OF TWINS 8:1

Estimated intensity	hkl	d_{hkl} Å.	$n\lambda$ Å.	S for $u=0.197$	$h'k'l'$	$d_{h'k'l'}$ Å.	$n'\lambda'$ Å.	S for $u=0.197$
0.8	$\bar{3}\bar{3}\bar{1}$	1.92	0.35	1.02	$\bar{7}.11.\bar{1}$	0.64	0.12	..
.9	$\bar{3}\bar{1}\bar{5}$	1.42	.32	0.82	$11.5.\bar{1}\bar{3}$.47	.11	..
1.3	$\bar{1}\bar{5}\bar{3}$	1.42	.35	.82	$5.\bar{1}\bar{3}.11$.47	.12	..
1.8	$\bar{3}\bar{5}\bar{1}$	1.42	.38	.82	$11.\bar{1}\bar{3}.5$.47	.13	..
0.05	$2\bar{2}\bar{1}$	2×1.40	$2 \times .43$.02	$\bar{4}\bar{8}\bar{1}$	$2 \times .47$	$2 \times .14$..
1.2	$0\bar{3}\bar{2}$	2×1.16	$2 \times .42$	1.99	$2\bar{7}\bar{8}$	$2 \times .39$	$2 \times .14$..
0.05	$\bar{3}\bar{4}\bar{1}$	2×0.83	$2 \times .43$	0.63	$13.\bar{8}.1$	$2 \times .28$	$2 \times .14$..
.3	$\bar{1}\bar{5}\bar{9}$.81	.43	1.80	$7.25.\bar{1}\bar{7}$.27	.14	..
.2	$\bar{1}\bar{3}.5.11$.47	.12	..	$5\bar{1}\bar{3}$	1.42	.37	0.82
.3	$\bar{1}\bar{3}.11.5$.47	.13	..	$5\bar{3}\bar{1}$	1.42	.39	.82

CRYSTAL NO. 2; INTENSITY RATIO OF TWINS 8:6; PHOTOGRAPH 1

0.6	$\bar{1}\bar{3}\bar{3}$	1.92	0.34	1.02	$\bar{1}.11.\bar{7}$	0.64	0.11	..
.6	$\bar{3}\bar{1}\bar{5}$	1.42	.29	0.82	$11.5.\bar{1}\bar{3}$.47	.10	..
2.5	$\bar{1}\bar{5}\bar{3}$	1.42	.41	.82	$5.\bar{1}\bar{3}.11$.47	.14	..
2.8	$\bar{3}\bar{5}\bar{1}$	1.42	.45	.82	$11.\bar{1}\bar{3}.5$.47	.15	..
0.2	$\bar{5}\bar{3}\bar{3}$	1.28	.33	.35	$17.\bar{7}.\bar{7}$.43	.11	..
1.8	$\bar{5}\bar{5}\bar{1}$	1.18	.32	2.65	$17.\bar{1}\bar{3}.\bar{1}$.39	.11	..
0.7	$30\bar{2}$	2×1.16	$2 \times .32$	1.99	$\bar{7}\bar{2}\bar{8}$	$2 \times .39$	$2 \times .11$..
.2	$2\bar{2}\bar{3}$	2×1.04	$2 \times .32$	1.22	$\bar{4}.\bar{4}.11$	$2 \times .35$	$2 \times .11$..
.5	$9\bar{1}\bar{5}$	0.81	.32	1.80	$\bar{1}\bar{7}.7.25$.27	.11	..
.02	$\bar{3}.11.\bar{3}$.71	.43	0.85	$19.\bar{2}\bar{3}.19$.24	.14	..
.06	$11.1.\bar{5}$.69	.43	2.16	$\bar{1}\bar{9}.11.29$.23	.14	..
.4	$11.\bar{7}.\bar{1}$.64	.10	..	$\bar{3}\bar{3}\bar{1}$	1.92	.30	1.02
1.0	$5.11.\bar{1}\bar{3}$.47	.12	..	$\bar{1}\bar{3}\bar{5}$	1.42	.35	0.82
1.7	$\bar{1}\bar{3}.5.11$.47	.13	..	$5\bar{1}\bar{3}$	1.42	.38	.82
2.0	$\bar{1}\bar{3}.11.5$.47	.14	..	$5\bar{3}\bar{1}$	1.42	.43	.82
0.03	$8\bar{1}\bar{4}$	$2 \times .47$	$2 \times .15$..	$\bar{2}\bar{1}\bar{2}$	2×1.40	$2 \times .45$.02
.7	$\bar{1}.17.\bar{1}\bar{3}$.39	.10	..	$\bar{1}\bar{5}\bar{5}$	1.18	.29	2.65
.3	$25.7.\bar{1}\bar{7}$.27	.15	..	$\bar{5}\bar{1}\bar{9}$	0.81	.44	1.80

CRYSTAL NO. 2; PHOTOGRAPH 2

0.05	$3\bar{7}\bar{5}$	0.92	0.42	0.24	$1.\bar{1}\bar{1}.25$	0.31	0.14	..
.4	$9\bar{3}\bar{1}$.88	.42	.04	$\bar{1}\bar{7}.19.13$.29	.14	..
.5	$9\bar{3}\bar{5}$.78	.43	.63	$\bar{1}\bar{3}.5.29$.26	.14	..
.06	$11.\bar{3}.\bar{1}$.73	.45	.32	$\bar{1}\bar{9}.\bar{2}\bar{3}.17$.24	.15	..
.05	$9\bar{7}\bar{5}$.68	.44	.75	$\bar{1}\bar{3}.35.\bar{1}$.23	.15	..
.15	$11.3.\bar{5}$.68	.43	.99	$\bar{1}\bar{5}.9.33$.23	.14	..

an increase in the relative reflecting power of Al will increase S for some planes and decrease it for others.

After the structure of $(\text{NH}_4)_3\text{AlF}_6$ had been determined, a crystal showing re-entrant angles was found. This crystal was shown by goniometric measurements to be twinned with (111) as twinning plane and composition plane. Sections of each of the two individuals were made parallel to the twinning plane by cleaving; Laue photographs of these sections showed the crystal axes to correspond to the twinning described above. Moreover, *no reflections requiring the larger unit were produced by either individual.* The data from these photographs were in agreement with the structure deduced above. Subsequent careful examination of the face development of the small crystal giving photographs with the 8:6 intensity ratio showed it to consist of two individuals twinned on (111); their thicknesses were in the same ratio, about 8:6.

The Structure of Ammonium Oxyfluomolybdate

Spectral data for ammonium oxyfluomolybdate, given in Table VI, place d_{111}/n equal to 5.25 Å. If n is 1, the unit of structure has $d_{100} = 9.10$ Å. No reflections were found on any of three Laue photographs which required a larger unit (on each photograph there were a few scattered spots close to the central image to which it was difficult to assign indices; these were explained as produced by a crystal fragment with an orientation different from that of the main crystal). The density calculated from the X-ray data, assigning four molecules to the unit, is 2.23 g./cc.; a direct determination by means of a pycnometer of the density of a liquid in which a small crystal remained suspended gave the value 2.28.

TABLE VI
SPECTRAL DATA FROM (111) OF $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$

Order of reflection	Line	Angle of reflection	d_{111}/n Å.	Estimated intensity
n	β	$3^\circ 26'$	5.26	ms
n	α	$3^\circ 53'$	5.25	vs
$2n$	a
$3n$	α	$11^\circ 44'$	5.24	vw
$4n$	α	$15^\circ 41'$	5.25	w

No planes were observed to give first-order reflections except those with all indices odd, indicating that the structure is based on a face-centered lattice. However, there are no arrangements of 4 Mo, 12 N, 12 O and 12 F based on this lattice,³ nor any which are approximately face-centered. If the oxygen and fluorine atoms are considered crystallographically equivalent, the possible structures are those discussed for $(\text{NH}_4)_3\text{FeF}_6$. The presence of a number of abnormal intensity relations eliminates 24(c). If the substance had the second arrangement, the observed intensities of

reflection from (111) would require that u be between 0.20 and 0.30. Throughout this region the structure factor for $\{551\}$ is over twice as great as that for $\{320\}$ ($n = 2$); the observation that the two forms reflect with about equal intensity accordingly eliminates this structure.

The spectral intensities from (111) limit the possible values of u for the third arrangement to the region between 0.15 and 0.30, with indications of a value near 0.20. The form $\{951\}$ reflected on Laue photographs as strongly as $\{755\}$, despite its smaller interplanar distance; this limits u to between 0.194 and 0.25 and the further observation that $\{755\}$ reflected more strongly than $\{931\}$ shows u to be less than 0.220. The values of S given in Table VII are calculated for $u = 0.21$.

TABLE VII
LAUE PHOTOGRAPHIC DATA FROM $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$, THROUGH (111)

hkl	d_{hkl} Å.	$n\lambda$ Å.	Estimated intensity	S for $u = 0.21$
$55\bar{1}$	1.27	0.28	0.20	4.09
$0\bar{2}3$	2×1.26	$2 \times .28$.20	3.42
$53\bar{7}$	1.00	.41	.08	1.23
$\bar{1}39$	0.95	.37	.04	2.28
$\bar{5}57$.91	.38	.05	2.86
$\bar{5}75$.91	.39	.05	2.86
159	.88	.41	.05	3.92
$3\bar{7}7$.88	.33	a	0.70
$\bar{5}93$.85	.34	.04	2.98

Discussion of the Structures

The arrangement of the atoms in the units of structure of ammonium fluoferrate, fluo-aluminate and oxyfluomolybdate is shown in Fig. 4.

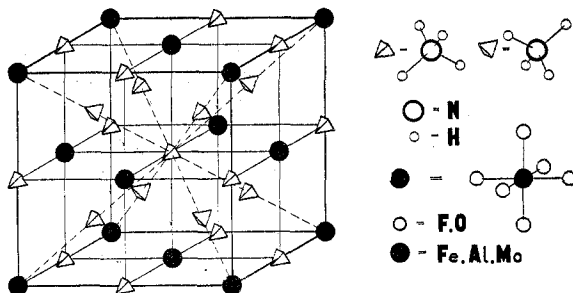


Fig. 4.—The arrangement of atoms in the units of structure of $(\text{NH}_4)_3\text{FeF}_6$, $(\text{NH}_4)_3\text{AlF}_6$ and $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$.

This arrangement is the same as that of ammonium chloroplatinate, chlorostannate and fluosilicate, except that four additional ammonium groups are introduced at $1/2^1/2^1/2$, $00^1/2$, $0^1/20$ and $1/200$.

The sum of the Bragg radii¹⁰ for iron and fluorine is 2.07 Å. The sum

¹⁰ Bragg, *Phil. Mag.*, 40, 180 (1920).

of the radii of molybdenum (taken¹¹ as 1.36) and fluorine is 2.03 Å., that of molybdenum and oxygen is 2.01. These distances are slightly larger than those tabulated in Table VIII. Moreover, the sum of the Bragg radii, 2.02 Å., is considerably larger than the Al to F distance in $(\text{NH}_4)_3\text{AlF}_6$. Bozorth has previously noted that the Si to F distance in $(\text{NH}_4)_2\text{SiF}_6$ is 1.72 Å., while the sum of the Bragg radii is 1.84. These deviations are illustrative of the lack of constancy of corresponding interatomic distances in crystals of different types.

TABLE VIII
INTERATOMIC DISTANCES FOR COMPLEX FLUORIDES

Substance	d_{100} Å.	u	M-F distance Å.	F-F distance Å.
$(\text{NH}_4)_3\text{FeF}_6$	9.10	0.21	1.9	5.3
$(\text{NH}_4)_2\text{MoO}_3\text{F}_3$	9.10	.21	1.9	5.3
$(\text{NH}_4)_3\text{AlF}_6$	8.40	.197	1.66	5.08
$(\text{NH}_4)_2\text{SiF}_6$ ^a	8.38	.205	1.72	4.94

^a Ref. 5.

The introduction of a third ammonium group expands the structure only slightly. The F to F distance along the crystal axes is only 0.14 Å.

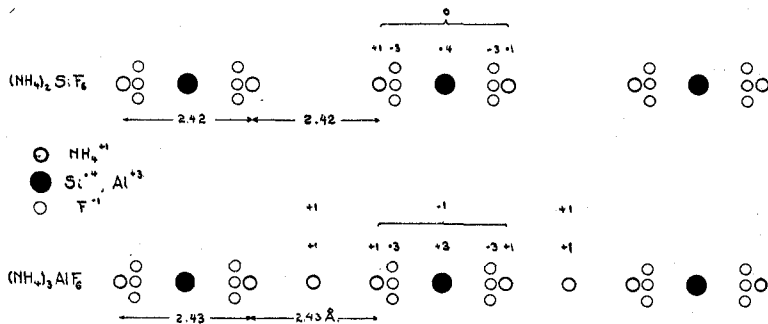


Fig. 5.—Diagrammatic representation of the sequence of planes of atoms along the normal to (111) of $(\text{NH}_4)_2\text{SiF}_6$ and $(\text{NH}_4)_3\text{AlF}_6$.

greater for ammonium fluo-aluminate than for the fluosilicate, despite the fact that for the former there is an ammonium group between the fluorine atoms.

No statement concerning the cleavage of these crystals has been found in the literature. Upon trial, ammonium oxyfluomolybdate and fluo-aluminate were found to have perfect octahedral cleavage. Crystals of the fluoferrate were not available for investigation. In the fluosilicate and isomorphous salts the atoms, presumably electrically charged to the extent indicated by their valences, are arranged in layers parallel to (111) as shown in Fig. 5. It is entirely reasonable to attribute the

¹¹ Dickinson and Pauling, *THIS JOURNAL*, **45**, 1466 (1923).

very complete octahedral cleavage of these crystals to the presence of electrically neutral layers separated by a relatively large distance. In the fluo-aluminate and salts isomorphous with it the corresponding groups have negative charges and midway between them lie positively charged layers. This change might be expected to reduce the ease with which cleavage occurs; direct comparison, however, showed that the fluo-aluminate cleaved approximately as readily as the fluosilicate and the chlorostannate.

It was not found possible to arrange 4 $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$ in a face-centered unit or in a unit approximately face-centered, except by assuming the oxygen and fluorine atoms to be in equivalent positions. These atoms probably have nearly but not exactly the same size. Moreover, their atomic numbers differ by one, so that if they have similar electron-shells the electrical charges on the entire atoms will differ by one. If they have not similar electron-shells, they differ in shape; they cannot be taken to be identical.

In the arrangement assigned to this crystal the MoO_3F_3 groups are at the intersection of four trigonal axes. But the group of three fluorine and three oxygen atoms around a molybdenum atom does not possess four trigonal axes. This apparent contradiction may have one of the following explanations.

(1) The true unit of structure may contain 32 molecules, or 256, or more. No Laue reflections were observed requiring a larger unit which, if it exists, must accordingly closely resemble a group of small units with the arrangement given. In view of this resemblance, it is difficult to understand how the MoO_3F_3 groups can, in the progress of crystallization, effect the proper orientation of other such groups depositing from solution 10 or 15 Å. away so as to arrange them in a manner completely concordant with the symmetry of the larger unit.

(2) It is conceivable, on the other hand, that the atoms of oxygen and of fluorine may be sufficiently similar to permit designating them as crystallographically equivalent in this case (not necessarily in all cases). The MoO_3F_3 group has approximately the form shown in Fig. 4. It is possible that in the formation of the crystals these groups are deposited with the oxygen and fluorine atoms directed at random along the crystal axes. Upon looking along a normal to an octahedral face of a crystal formed in this way one would see on the average the same number of oxygen atoms (and fluorine atoms) in the direction of each of the crystal axes. If this is the way in which a crystal of $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$ is built, the unit of structure is that shown in Fig. 4. The crystal will at points within it show slight distortions; since these distortions are random ones, they will not affect the symmetry of the crystal as a whole.

Some justification for the belief in this hypothesis is afforded by the

existence of solid solutions between isomorphous crystals. A bromine atom differs considerably from a chlorine atom; however, in the formation of solid solutions of potassium bromide and chloride, replacements of one by the other occur, apparently at random.¹² It is evident that in the case of such a solid solution distortions similar to those presumed to occur in $(\text{NH}_4)_3\text{MoO}_3\text{F}_3$ are present, and that the symmetry of the entire atomic arrangement is retained because of the random distribution of the distortions. For the solid solutions which show simple stoichiometrical relations between the amounts of the constituents present, the formation of larger units of structure may be invoked in explanation, as in (1), but this cannot be done in general.

Summary

Cubic crystals of ammonium fluoferrate, fluo-aluminate and oxyfluomolybdate have been prepared and their structures determined by means of data from spectral, Laue and powder photographs interpreted with the aid of the theory of space groups. The units of structure, based on a face-centered lattice, contain four molecules. The arrangement of atoms within the units is shown in Fig. 4 and the values determined for d_{100} and the parameter u are given in Table VIII.

The structures of these crystals are closely related to those of ammonium chlorostannate and isomorphous salts; the crystals likewise show very good octahedral cleavage.

In interpreting the data for ammonium oxyfluomolybdate, atoms of oxygen and fluorine were considered to be crystallographically equivalent, arguments being given in justification of this supposition.

PASADENA, CALIFORNIA

NOTE

Effect of Pressure on Overvoltage.—A recent article by Bircher and Harkins¹ on the effect of pressure on overvoltage gives results quite divergent from those of Goodwin and Wilson.² Some measurements of the author are in concordance with the results of Bircher and Harkins, and it is felt that they are worth publishing in order to give weight to what appear to be the correct data.³

Bircher and Harkins concluded that the hydrogen overvoltage on lead, mercury and nickel increases with decrease in pressure from 760 mm. to 11 mm. by the same amount that the reversible hydrogen electrode potential decreases with pressure decrease. Thus the cathode potential,

¹² Vegard, *Z. Physik*, **5**, 17 (1921).

¹ Bircher and Harkins, *THIS JOURNAL*, **45**, 2890 (1923).

² Goodwin and Wilson, *Trans. Am. Electrochem. Soc.*, **40**, 172 (1921).

³ These data were obtained in 1922 but were delayed in publication.