the intensities of the reflexions of the two compounds are rather similar as Table 1 shows.

To complete the similarities, the indexing of $FeVO_4$ (given by Young & Schwartz) has to be reconsidered. It was found by Panagos (1963) that the disordered $FeNbO_4$ crystallizes in the space group *Pbcn* (D_{2h}^{14}) (referring to the axes chosen above). The following reflexions should be absent:

$hk0$ with $h+k$ odd
$0kl$ with k odd
$h0l$ with l odd .

This means that 032, 140 and 212 (in the setting of Young & Schwartz indexed as 023, 104 and 221) should not reflect. Within the accuracy of the measurements reported by Young & Schwartz, 032 can be interpreted as 113, and 212 as 221.

There remains the questionable reflexion in the $FeVO_4$ indexing, namely $d=1\cdot323$ Å which was indexed as 104 (140 in the Laves setting). The calculation of the orthorhombic axes was based on some high-order reflexions. With some ambiguity in indexing of the powder pattern, the cell dimensions may have been incorrect. If the 1·323 line is indexed as 041 and the 1·383 line as 311 in the Laves indices, a good fit to these and the other reflexions is obtained with orthorhombic axes

$$a, b, c=4\cdot49,\ 5\cdot51,\ 4\cdot85\ .$$

With this revision in indexing and axes, the indexing of the high-pressure $FeVO_4$ and the disordered wolframite $FeNbO_4$ are in close agreement.

Thus it seems very probable that the high-pressure form of $FeVO_4$ crystallizes in the disordered wolframite type and that therefore vanadium would indeed have also in $FeVO_4$ the coordination number 6 as suggested by Young & Schwartz.

The similar structure of the high-pressure $FeVO_4$ and the ambient pressure $FeNbO_4$ is of interest because it offers another example of a high-pressure oxide with the same type of structure as an ambient-pressure oxide obtained by replacing one of the cations with the next element in the periodic group or subgroup. Other examples of such high-pressure — ambient-pressure pairs are rutile-type $CrVO_4$ and $CrNbO_4$ (Young & Schwartz, 1962); rutile-type SiO_2 and GeO_2 (Stishov & Popova, 1961); rutile-type $AlAsO_4$ and $AlSbO_4$ (Young, Sclar & Schwartz, 1963); the wolframite-type molybdates, $MgMoO_4$, $ZnMoO_4$, $MnMoO_4$, $FeMoO_4$, $CoMoO_4$, $NiMoO_4$ and the corresponding tungstates (Young & Schwartz, 1963); rock-salt-type ZnO and CdO (Bates, White & Roy, 1962).

The experimentational high-pressure work was done by A.P.Y. and C.M.S. under Air Force Office of Scientific Research Contract No. AF 49/638)–441. F. Laves thanks Ciba A. G., Basel, for financial support of the work on $FeNbO_4$.

References

Bates, C. H., White, W. B. & Roy, R. (1962). *Science*, **137**, 993.
Keeling, R. O. (1957). *Acta Cryst.* **10**, 209.
Laves, F., Bayer, G. & Panagos, A. (1963). *Schweiz. Min. Petrogr. Mitt.* **43**, 217.
Panagos, A. (1963). Thesis, E.T.H., Zürich. (In the press.
Stishov, S. M. & Popova, S. V. (1961). *Geokhimia*, **10**, 837.
Young, A. P. & Schwartz, C. M. (1962). *Acta Cryst.* **15**, 305.
Young, A. P. & Schwartz, C. M. (1963). *Science*, **141**, 348.
Young, A. P., Sclar, C. B. & Schwartz, C. M. (1963). *Z. Kristallogr.* **118**, 223.

Acta Cryst. (1964). **17**, 1477

The structure of a new phase of aluminum trifluoride monohydrate.

By Ronald Chandross, *Allied Chemical Corp., General Chemical Research Laboratory, Morristown, New Jersey, U.S.A.*

(*Received* 18 *May* 1964)

Introduction

The system of aluminum trifluoride hydrates is a difficult one to work in because of its tendency to form compounds of dubious stoichiometry. While several higher hydrates have been prepared and studied (Fischer & Bock, 1950; Freeman, 1956, 1957) the only report of a monohydrate is the mineral fluellite (Wolfe, 1945), whose existence is apparently in doubt. This report describes the structure of a fortuitously prepared material which appears to be a clean phase of $AlF_3.H_2O$.

Preparation of specimen

The $AlF_3.H_2O$ appeared as an insoluble, white precipitate at the bottom of an industrial scrubbing column. In this column, a dilute (*ca.* 2%) HF gas stream was passed countercurrently through a solution of $AlCl_3$ (*ca.* 5%) in constant-boiling hydrochloric acid. Several attempts were made to duplicate the synthesis on a laboratory scale, but they all failed. The powder was air dried and analyzed directly for aluminum and fluoride ion, and the water was obtained by thermal drying. Trace amounts ($<1\%$) of chloride ion were also present. A powder diffraction pattern showed the powder to consist of a cubic material, plus a few barely discernible lines of $AlCl_3$. The material that had been ignited in the determination of the water of hydration gave the characteristic powder pattern of AlF_3. The density of the original material was determined by suspension in a mixture of diiodomethane and acetone, and found to be $2\cdot45\pm0\cdot02$ g.cm^{-3}.

Determination of structure

The powder pattern consisted of a series of lines from a single cubic lattice, plus the few impurity lines. An extrapolation of a *versus* $\frac{1}{2}(\cos^2\theta/\sin\theta+\cos^2\theta,\theta)$ to 180° gave a lattice parameter of 3·610 Å. This, combined with the density, leads to one formula weight per unit cell. However, upon lengthy exposure, interspersed between these primary lines, was a set of barely discernible (invisible to a diffractometer) lines. These lines can be accounted for if the pattern is reindexed with the parameter doubled.

Table 1. *Observed and calculated structure factors*

hkl	I^*(obs.)	F(obs.)	F(calc.)
100	10,000	14·8	15·7
(110)	0	0	(0)
111	1,324	9·2	−5·9
200	3,689	22·2	28·5
210	2,853	11·6	12·0
211	133	2·7	2·1
220	1,354	16·7	20·5
(221)			
(300)	944	9·7	9·6
222	363	14·2	16·3
320	308	7·9	8·0
321	118	3·6	2·3
400	190	13·1	13·7
(322)			
(410)	659	8·5	7·1
(330)			
(411)	192	5·0	2·2
420	837	11·6	13·2
421	1,134	7·9	8·2

* Arbitrary scale.

The integrated intensities were measured with Cu $K\alpha$ radiation by scanning with a Norelco diffractometer. The observed intensities are shown in Table 1. The indexing is on the basis of the 3·610 Å unit cell, the extremely weak secondary lines being ignored at this point. It will be observed that the 110 line is conspicuously absent.

On the basis of the lack of systematic absences and the one formula weight per unit cell, the space group can be assigned as $Pm3m$ (O_h^1). From the usual structural considerations, one would anticipate that the Al^{3+} would be at the center of a cube, and the F^- ions at the face centers, and the water molecule distributed in some fashion within the cell. In order to find this distribution, it is necessary only to find the parameters that will cause the 110 line to vanish. If one tries various possibilities, it soon becomes clear that if (for convenience) the Al^{3+} is placed in 1(*a*) (0, 0, 0), the only combination that permits F_{110} to be zero, and gives reasonable intensity agreement of the strong lines, is to put the F^- in 3(*d*) ($\frac{1}{2}, 0, 0;\ 0, \frac{1}{2}, 0;\ 0, 0, \frac{1}{2}$) and to distribute randomly (*i.e.*, place $\frac{1}{3}$) of the water molecule in 3(*c*) ($0, \frac{1}{2}, \frac{1}{2};\ \frac{1}{2}, 0, \frac{1}{2};\ \frac{1}{2}, \frac{1}{2}, 0$). The F_{hkl}'s calculated on this basis are shown in Table 1. The F_{hkl}'s were calculated by assuming a temperature factor $B=2·0$ for the Al^{3+} and F^-, and $B=4·0$ for the O^{2-} ions. A scale factor was found by calculating $\langle F(\mathrm{cal})/F(\mathrm{obs})\rangle$. The final R index on the basis of all measured reflections is 16·4%.

Conclusions

$AlF_3.H_2O$ forms a cubic lattice, with the Al^{3+} at the body center of the cube and the fluoride ions at the face centers. The observed Al^{3+}–F^- distance (1·805 Å) is in good agreement with that reported by Naray-Szabo & Sasvari (1938) for the $[AlF_6]^{3-}$ anion (1·81 Å). The one water molecule is randomly distributed at the centers of the cube edges. There is apparently some correlation among the water molecules of the unit cells. This correlation is strong enough to appear to double the size of the unit cell, giving rise to weak superstructure lines. If the intensities of these faint lines were measured, the degree of order in the compound could be determined.

I would like to thank Mr L. V. Haff for providing me with this compound, and Mr Howard McGee for aiding in measuring the intensities and in the calculations.

References

Fischer, V. W. & Bock, E. (1950). *Z. anorg. Chem.* **262**, 54.
Freeman, R. D. (1956). *J. Phys. Chem.* **60**, 1152.
Freeman, R. D. (1957). *J. Phys. Chem.* **61**, 256.
Wolfe. (1945). Quoted in *Dana's System of Mineralogy*, 7th Ed. **2**, 124.
Naray-Szabo, I. & Sasvari, K. (1938). *Z. Kristallogr.* **99**, 27.

Acta Cryst. (1964). **17**, 1478

The crystal structure of Tutton's salts. II. Magnesium ammonium sulfate hexahydrate and nickel ammonium sulfate hexahydrate.

By H. Montgomery, *Canadian Services College, Royal Roads, Victoria, B. C., Canada* and E. C. Lingafelter, *Department of Chemistry, University of Washington, Seattle, Washington* 98105, *U.S.A.*

(*Received* 15 *June* 1964)

In the course of a series of investigations on Tutton salts (Montgomery & Lingafelter, 1964) the structures of magnesium ammonium and nickel ammonium sulfate hexahydrate $(NH_4)_2Mg(SO_4)_2.6H_2O$ and $(NH_4)_2Ni(SO_4)_2.6H_2O$ have been determined from three-dimensional X-ray diffraction data with Cu $K\alpha$ radiation ($\lambda=1·5418$) and refined by a least-squares procedure. The structures have already been reported elsewhere (Mg, Margulis & Templeton, 1962; Ni, Grimes, Kay & Webb, 1963), but a brief account of the present results is given since the previously published structure of the nickel salt was based on two-dimensional data.

Magnesium salt

Cell dimensions (calibrated with a_0 for NaCl = 5·6387 Å)

$$a = 9·383 \pm 0·015,\quad b = 12·669 \pm 0·02,\quad c = 6·220 \pm 0·005 \text{ Å};\quad \beta = 107°\ 03' \pm 6'.$$