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On the high-pressure form of $FeVO_4$.

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In a note on high-pressure forms of $CrVO_4$ and $FeVO_4$ Young & Schwartz (1962) report that $CrVO_4$ occurs in the rutile-type structure and that $FeVO_4$ occurs in an orthorhombic structure. It was suggested that the atomic arrangement of the high-pressure $FeVO_4$ might be somewhat related to the rutile type. However, a more probable explanation is that the high-pressure form of $FeVO_4$ reported on crystallizes in a disordered wolframite type.

In a thesis (Panagos, 1963) and in additional work (Laves, Bayer & Panagos, 1963) it was found that $FeNbO_4$ occurs in three modifications: monoclinic (pseudo-orthorhombic) wolframite type (Fe and Nb ordered, space group $P2/c$ (C_{2h}^4)) $\rightarrow$ orthorhombic disordered wolframite type (Fe and Nb disordered, space group $Pbcn$ (D_{2h}^{14})) $\rightarrow$ rutile type (Fe and Nb disordered), the rutile type being the stable modification at high temperature.

If one chooses the axes a, b, c of the disordered orthorhombic $FeNbO_4$ in accordance with the traditional (ordered) wolframite setting (Keeling, 1957), the orthorhombic axes are

$$a, b, c \text{ and } a:b:c = 4{\cdot}66,\ 5{\cdot}62,\ 5{\cdot}01 \text{ and } 0{\cdot}83:1:0{\cdot}89\ .$$

If the Young & Schwartz (1962) setting for $FeVO_4$ ($a, b, c = 4{\cdot}49, 4{\cdot}90, 5{\cdot}53$) is changed by exchanging the b and c axes, their values are

$$a, b, c \text{ and } a:b:c = 4{\cdot}49,\ 5{\cdot}53,\ 4{\cdot}90 \text{ and } 0{\cdot}81:1:0{\cdot}89\ .$$

This already shows a close resemblance. In addition, considering the different scattering powers of Nb and V,

Table 1. *Indexing* of high pressure* $FeVO_4$ *and normal pressure* $FeNbO_4$ (*re* Fe *and* Nb *disordered wolframite type*)

1 Indices after Young & Schwartz $a = 4{\cdot}491$† $b = 4{\cdot}900$† $c = 5{\cdot}530$†	2 Indices* using $a = 4{\cdot}491$ $b = 5{\cdot}530$ $c = 4{\cdot}900$ ($Pbcn$)	3 d_c ($FeVO_4$) using $a = 4{\cdot}491$† $b = 5{\cdot}540$† $c = 4{\cdot}840$†	4 d_o ($FeVO_4$)	5 d ($FeVO_4$) minus d ($FeNbO_4$)	6 d ($FeVO_4$) using $a = 4{\cdot}658$ $b = 5{\cdot}624$ $c = 5{\cdot}011$ ($Pbcn$)	7 Int ($FeVO_4$)	8 Int ($FeNbO_4$)
101	110	3·490	3·48	0·11	3·59	50	32
111	111	2·831	2·83	0·09	2·92	100	100
002	020	2·770	2·77	0·04	2·81	30	11
020	002	2·420	2·42	0·09	2·51	20	9
012	021	2·404	2·40	0·05	2·45	20	13
200	200	2·247	2·242	0·09	2·33	< 5	4
	102	2·131			2·21		4
112	121	2·120	2·119	0·05	2·17	40	9
121	112	1·989	1·991	0·06	2·05	10	8
211	211	1·913	1·915			5	
022	022	1·822	1·823	0·05	1·87	20	8
202	220	1·745	1·741	0·05	1·79	15	6
103	130	1·708	1·704	0·04	1·74	30	14
220	202	1·647	1·648	0·06	1·71	15	13
212‡	221	1·642	1·640	0·04	1·68	40	21
113	131	1·611	1·610			< 5	
131	113	1·464	1·466	0·04	1·51	20	11
	222	1·415			1·46		4
123	132	1·396	1·396	0·03	1·428	30	13
	023	1·394		0·04	1·435		
	311	1·386	1·383			15	
004	040	1·385					
	041	1·332	1·323	0·03	1·354	15	5
104	140§	1·324					
231	213	1·275	1·276			< 5	
	312	1·241		0·04	1·285		2
040	004	1·210	1·212	0·04	1·253	< 5	1

* With one exception — 140 — only those reflexions which conform with $Pbcn$ are used in the table. However, the reflexions 122, 212, 310, 231, 123, 141, 302, 321, 232 which could occur in $Pbcn$ but were not observed either with $FeVO_4$ or with $FeNbO_4$ have been omitted.

† The a, b, c values of column 1 were given by Young & Schwartz in their note as lattice constants of $FeVO_4$. However, in their Table 2, $d(020)_c$ and $d(002)_c$ were given as 2·42 and 2·77 and compared with the corresponding d_o values 2·42 and 2·77. Thus, for the d-values calculated in column 3 values $2 \times 2{\cdot}42 = 4{\cdot}840$ and $2 \times 2{\cdot}77 = 5{\cdot}540$ were used.

‡ For this reflexion Young & Schwartz gave the indices 221, obviously a misprint.

§ This 'questionable' reflexion has been included despite the fact that it should be extinct (*cf.* the discussion in the text).

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:

$$\begin{array}{lll} hk0 & \text{with} & h+k \text{ odd} \\ 0kl & \text{with} & k \text{ odd} \\ h0l & \text{with} & l \text{ odd} . \end{array}$$

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).

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The structure of a new phase of aluminum trifluoride monohydrate.

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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 $2\cdot45 \pm 0\cdot02$ $g.cm^{-3}$.