atoms, 2·757 and 2·759 A. in MoF_3 and TaF_3 respectively, is not inconsistent with the accepted value of 1·36 A. for the fluorine ionic radius, but since the metal atoms will probably force the non-metal atoms apart, the effective size of the fluorine atoms in these structures cannot be deduced from their distances of closest approach.

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The Crystal Structure of Vanadium Trifluoride, VF_3

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The unit cell of vanadium trifluoride, VF_3, is rhombohedral with dimensions $a = 5{\cdot}373 \pm 0{\cdot}002$ A., $\alpha = 57{\cdot}52 \pm 0{\cdot}03°$. The structure places atoms in the following special positions of space group $R\bar{3}c$:

$$2\ \text{V atoms at}\ 0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2},\ \text{and}$$

$$6\ \text{F atoms at}\ \pm(x, \tfrac{1}{2}-x, \tfrac{1}{4});\ \pm(\tfrac{1}{2}-x, \tfrac{1}{4}, x);\ \pm(\tfrac{1}{4}, x, \tfrac{1}{2}-x),$$

with $x = -0{\cdot}145 \pm 0{\cdot}015$ Direct experimental evidence shows that the structural unit is not the unimolecular rhombohedron proposed by some workers for the isomorphous FeF_3, CoF_3, RhF_3 and PdF_3. Preliminary observations indicate that CoF_3 has a bimolecular unit cell and is isostructural with VF_3. The VF_3 structure is not identical either to that of AlF_3 or to that of the ScF_3, MoF_3 and TaF_3 group, but has relationships with each of these structure types. Almost regular octahedra of fluorine atoms, each with a vanadium atom at its centre, are joined by sharing corners only. The fluorine atoms are not close-packed, and although their arrangement approximates to a hexagonal close-packing rather than to a cubic close-packing, it can be derived from the latter by relatively small atomic movements and by omission of atoms from certain sites. Principal interatomic distances are

$$\text{V–V} = 3{\cdot}73;\quad \text{F–F} = 2{\cdot}74\ \text{and}\ 2{\cdot}75;\quad \text{V–F} = 1{\cdot}95\ \text{A.}$$

Introduction

Vanadium trifluoride, VF_3, was first prepared by Ruff & Lickfett (1911) by the action of anhydrous hydrogen fluoride on vanadium trichloride at red heat. The present X-ray work is the first on this fluoride and was carried out on pure specimens obtained in a recent chemical investigation (Emeléus & Gutmann, 1949) with which one of us was associated.

Preliminary observations suggested that VF_3 is isostructural with the trifluorides of iron, cobalt, rhodium and palladium, but since the structures of these are not yet fully established (see Wyckoff, 1948, section 1, chap. 5, text p. 13) a complete investigation of the vanadium compound seemed desirable. The structures proposed for FeF_3, CoF_3, RhF_3 and PdF_3 by Ebert (1931) (*Strukturbericht*, 1937 *a*, *b*) were based solely upon spatial and symmetry considerations and are found to be incompatible with the observed intensities of X-ray reflexions. All observed reflexions were indexed on a rhombohedral cell containing only one molecule, but the proposed structure requires a larger bimolecular unit cell, space group $R\bar{3}c$, the dimensions of which are given in Table 1. The given parameters, i.e.

$$2\ \text{metal atoms at}\ 0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2},\ \text{and}$$

$$6\ \text{F atoms at}\ \pm(x, \tfrac{1}{2}-x, \tfrac{1}{4});\ \pm(\tfrac{1}{2}-x, \tfrac{1}{4}, x);\ \pm(\tfrac{1}{4}, x, \tfrac{1}{2}-x),$$

with $x = -\tfrac{1}{12}$, indicate a slightly distorted hexagonal close-packing of the fluorine atoms with the metal atoms occupying certain octahedral interstices and forming a rhombohedrally distorted simple-cubic superlattice. The structure of aluminium trifluoride has been

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Table 1. *Cell dimensions of some trifluorides*

(Values are in Ångström units and where necessary have been converted from the kX. units given in the literature by multiplying by 1·00202. Dimensions of the true structural units are given in clarendon figures.)

	Unimolecular rhombohedron		Bimolecular rhombohedron		Hexagonal pseudo-cell		
	a	*α*	*a*	*α*	*a*	*c*	Author
AlF_3	3·523	88·67	**5·039**	**58·52**	4·924	12·485	Ketelaar (1933)
VF_3	3·729	87·80	**5·373**	**57·52**	5·171	13·403	Present work
FeF_3	3·764	88·24	5·372	58·04	5·212	13·35	Ebert (1931)
CoF_3	3·671	87·33	**5·310**	**57·04**	5·071	13·29	Ebert (1931)
RhF_3	3·624	84·80	5·354	54·32	4·888	13·65	Ebert (1931)
PdF_3	3·760	84·65	5·560	54·17	5·063	14·19	Ebert (1931)
ScF_3	**4·030**	**89·58**	5·720	59·52	5·678	7·031	Nowacki (1939)
MoF_3	**3·8985**	**90·00**	5·513	60·00	5·513	6·752	Gutmann & Jack (1951)
TaF_3	**3·9012**	**90·00**	5·517	60·00	5·517	6·757	Gutmann & Jack (1951)

established beyond reasonable doubt by Ketelaar (1933), who claimed that it was probably isomorphous with the FeF_3 group of fluorides. The bimolecular unit cell of AlF_3, space group $R32$, contains

2 Al atoms at $\pm(u, u, u)$, with $u = 0{\cdot}237$,

3 F atoms at $0, v, \bar{v};\ v, \bar{v}, 0;\ \bar{v}, 0, v$, with $v = 0{\cdot}430$,

and

3 F atoms at $\frac{1}{2}, w, \bar{w};\ w, \bar{w}, \frac{1}{2};\ \bar{w}, \frac{1}{2}, w$, with $w = 0{\cdot}070$.

These parameters place the fluorine atoms in considerably distorted hexagonal close-packing. The FeF_3 structure proposed by Ebert may be referred to the less symmetrical space group $R32$ with parameters $u(\text{Fe}) = 0{\cdot}250$, $v(\text{F}) = 0{\cdot}333$, and $w(\text{F}) = 0{\cdot}167$, which differ quite markedly from Ketelaar's AlF_3 values. From spatial considerations, a suggestion was made by Wooster (1933) that the group of transition element trifluorides had distorted ReO_3 structures. This was shown to be true by Nowacki (1939) for scandium trifluoride, which has a rhombohedral unit cell (pseudo-cubic; see Table 1), space group $R32$, containing

1 Sc at 0, 0, 0, and

3 F at $\frac{1}{2}, x, \bar{x};\ x, \bar{x}, \frac{1}{2};\ \bar{x}, \frac{1}{2}, x$,

with $x = 0{\cdot}027 \pm 0{\cdot}003$. The ScF_3 structure is a slightly distorted form of the MoF_3 and TaF_3 structures (Gutmann & Jack, 1951) in which the fluorine atoms have a cubic close-packing. Although Wooster's and Nowacki's suggestion has been widely quoted (e.g. see Wells, 1945, p. 275), Wyckoff (1948, section 1, chap. 5, text p. 11) concludes that it is not certain whether the correct structural units for the trifluorides are the unimolecular pseudo-cubes or the larger bimolecular rhombohedral cells.

In the present investigation, direct evidence obtained by the use of monochromatic X-radiation shows that the contents of the rhombohedral unit cell of vanadium trifluoride are V_2F_6. Each vanadium atom is at the centre of an almost regular octahedron of six fluorine atoms which is joined to similar co-ordination octahedra by sharing corners only. The fluorine atoms are not close-packed and their arrangement is not identical with that of AlF_3 nor with the various fluorine atom arrangements for FeF_3, CoF_3, RhF_3 and PdF_3 proposed by previous workers and based upon inadequate data.

Experimental

Preliminary powder photographs obtained with filtered Cu $K\alpha$ radiation showed a high background intensity due to fluorescent X-radiation. All measurements were therefore made on negatives obtained with crystal-reflected Cr $K\alpha$ radiation (α_1, 2·28962; α_2, 2·29352 A.) from a lithium fluoride monochromator. Observed and calculated intensities and unit-cell dimensions were found by methods previously described (Gutmann & Jack, 1951).

Results

Reflexions observed on 19 cm. powder photographs of VF_3 taken with filtered Cu $K\alpha$ radiation were all indexed on a unimolecular rhombohedral unit cell of dimensions $a = 3{\cdot}729$ A., $\alpha = 87{\cdot}80°$. With Cr $K\alpha$ monochromatic radiation the photographs had a low background intensity and this, together with the increased resolution due to the longer X-ray wave-length, disclosed additional reflexions which could not be indexed on the simple cell. As shown in Table 2, all reflexions were finally indexed on a unit cell of dimensions

$$a = 5{\cdot}373 \pm 0{\cdot}002 \text{ A.},\ \alpha = 57{\cdot}52 \pm 0{\cdot}03°,$$

and with contents V_2F_6; observed density 3·36 (Ruff & Lickfett, 1911), calculated density 3·46 g.cm.$^{-3}$. General considerations indicated that it was necessary to consider only the space groups $R32$ (cf. AlF_3; Ketelaar, 1933) and $R\bar{3}c$ (cf. FeF_3; *Strukturbericht*, 1937*a*, *b*). Excellent agreement (see Table 2) was obtained between observed and calculated intensities by placing the atoms in the following positions of $R\bar{3}c$:

2 V atoms at $0, 0, 0;\ \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, and

6 F atoms at $\pm(x, \frac{1}{2}-x, \frac{1}{4});\ \pm(\frac{1}{2}-x, \frac{1}{4}, x);\ \pm(\frac{1}{4}, x, \frac{1}{2}-x)$,

with $x = -0{\cdot}145 \pm 0{\cdot}015$. For comparison with AlF_3 the structure may be referred to space group $R32$, in which case the origin is shifted by $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and the atomic co-ordinates become

2 V atoms at $\pm(u, u, u)$, with $u = 0{\cdot}250$,

3 F atoms at $0, v, \bar{v};\ v, \bar{v}, 0;\ \bar{v}, 0, v$, with $v = 0{\cdot}395$,

3 F atoms at $\frac{1}{2}, w, \bar{w};\ w, \bar{w}, \frac{1}{2};\ \bar{w}, \frac{1}{2}, w$, with $w = 0{\cdot}105$.

The parameters (see Table 3) are approximately midway between those for AlF_3 and those giving an almost perfect hexagonal close-packing of fluorine atoms, as in the incorrectly proposed structure for FeF_3.

Table 2. *Calculated and observed X-ray data for vanadium trifluoride*

(Cr $K\alpha$ radiation.)

	$\sin^2\theta$		Relative intensities		
hkl	Calc.†	Obs.	Calc.		Obs.
110	0·0950	0·0949	156		164
211	0·1828	0·1829	23		24
$1\bar{1}0$	0·1969	0·197	4		5
*210	0·2626	0·2628	95	99	96
222	0·2635		4		
200	0·2915	—	1		0
220	0·3792	0·3793	74		77
321	0·4598	0·4601	113		117
$21\bar{1}$	0·4877	0·4877	40		42
332	0·5334	0·5336	8		8
310	0·5754	0·575	26		29
$2\bar{1}\bar{1}$	0·5894	0·590	57		52
*320	0·6410	0·641	13		14
422	0·7295	0·7294	37		36
$2\bar{2}0$	0·7855	0·787	9	46	48
*432	0·7882		37		
433	0·7960	0·7960	24		23
*421	0·8161	0·815	13		12
*$31\bar{1}$	0·8511	0·855	18	51	50
330	0·8520		0·04		
411	0·8520		0·04		
*$2\bar{2}1$	0·8581		33		
$3\bar{1}0$	0·8800	0·8799	90		92
431	0·9256	0·925	10		16

* Reflexions require a bimolecular unit cell.
† Values calculated from the cell dimensions and corrected for systematic errors.

Table 3. *Comparison of parameters for trifluorides referred to space group R32*

	u (*M*)	*v* (F)	*w* (F)	Author
AlF_3	0·237	0·430	0·070	Ketelaar (1933)
VF_3	0·250	0·395	0·105	Present work
FeF_3, CoF_3, RhF_3, PdF_3	0·250	0·333	0·167	Ebert (1931)

It should be noted in Table 2 that the six X-ray reflexions marked with an asterisk have $h+k+l$ odd and therefore cannot be accounted for by a unimolecular rhombohedral unit cell. Only two of these, the relatively weak (320) and (421) reflexions, do not overlap with reflexions for which $h+k+l$ is even. If this is also true for iron, cobalt, rhodium and palladium trifluorides, it is not surprising that there has been some confusion as to their true structural units. The remaining four 'bimolecular' reflexions are strong and overlap very weak 'unimolecular' reflexions. In previous work (Ebert, 1931) such reflexions have been incorrectly indexed so that the structures proposed are necessarily inconsistent with the experimental data. Using the more refined X-ray techniques of the present work, preliminary observations indicate that cobalt trifluoride is isostructural with vanadium trifluoride.

Discussion of the VF_3 structure and its relationship with other trifluoride structures

The VF_3 structure consists of alternate and regularly spaced planes of vanadium and planes of fluorine atoms perpendicular to the [111] direction. In AlF_3 the fluorine planes are equally spaced, but the aluminium planes are not. This difference between the two fluorides is illustrated in Fig. 1. Each fluorine atom of VF_3 is surrounded in its own plane by six other fluorine atoms, four at 2·75 A. and two at 3·54 A., and has six fluorine neighbours in adjacent fluorine planes, four (two in the plane above and two below) at 2·74 A. and two (one above and one below) at 3·08 A. Each vanadium atom occupies the centre of an octahedron formed by six fluorine neighbours—three in the plane above and three below, and each at a distance of 1·94 A. Each octahedron is almost regular, having six of its edges 2·75 A.

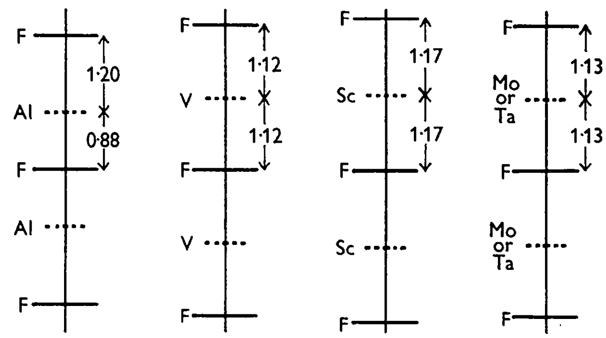

Fig. 1. Successive metal-atom planes and fluorine-atom planes, perpendicular to [111], in AlF_3, VF_3, ScF_3, MoF_3 and TaF_3.

and the remaining two 2·74 A. It is joined to other co-ordination octahedra by sharing corners only. The vanadium atoms form a rhombohedrally distorted simple cubic lattice ($\alpha = 87{\cdot}8°$) in which each atom is at 3·73 A. from its six metal-atom neighbours. Fig. 2 is a projection of the structure in the [111] direction and shows twelve successive planes. The arrangement of fluorine atoms may be regarded as a considerably distorted hexagonal close-packing with particularly large interstices at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ and $\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$. The centres of these 'holes' are co-ordinated by nine fluorine atoms, six at 2·74 A. and three at 2·04 A. Thus each 'hole' is almost large enough to accommodate an additional fluorine atom. The structure therefore contains only three-quarters of the number of fluorine atoms which might be expected for perfect close-packing. This feature is analogous with that found in MoF_3 and TaF_3 in which only three-quarters of the possible cubic close-packed fluorine sites are filled. Indeed, the VF_3 structure may be regarded as a distorted ReO_3 pseudo-cube with the fluorine atoms displaced from the mid-points of the cell edges by 0·54 A. The movements necessary to bring the atoms of three successive fluorine planes into these cubic close-packed sites are indicated in Fig. 2 by short arrows.

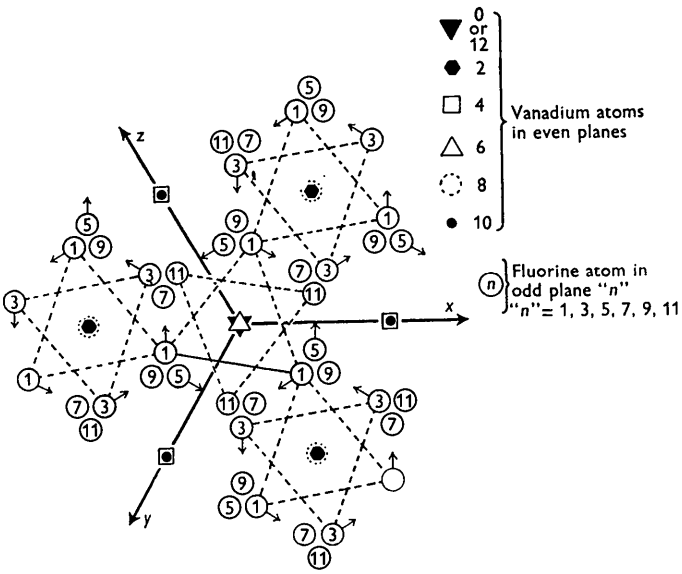

Fig. 2. Projection of the VF_3 structure in the [111] direction. V atoms in even planes 0–12; F atoms in odd planes 1–11.

Table 4. *Interatomic distances for known trifluorides*

(Co-ordination numbers are given in parentheses. Values are in Ångström units.)

	AlF_3	ScF_3	VF_3	MoF_3	TaF_3
M–*M*	(3) 3·35 (3) 3·73	(6) 4·03	(6) 3·73	(6) 3·90	(6) 3·90
F–F	(4) 2·54 (4) 2·58	(2) 2·72 (4) 2·86 (2) 3·03	(4) 2·74 (4) 2·75	(8) 2·76	(8) 2·76
M–F	(3) 1·71 (3) 1·89	(6) 2·02	(6) 1·94	(6) 1·95	(6) 1·95

In conclusion, the structure of vanadium trifluoride is not identical either to that of AlF_3 or to that of the ScF_3, MoF_3 and TaF_3 group, but has relationships with each of these structure types. Interatomic distances in the trifluorides of known structure are listed in Table 4.

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