

Table 1. Guinier powder pattern of Nb₃O₇F (CuK α ₁ radiation).

hkl	$\sin^2\theta_{\text{obs}}$	$\sin^2\theta_{\text{calc}}$	I_{obs}
0 1 1	1954	1951	w
0 2 0	2148	2146	w
1 0 0	3853	3846	v st
0 0 2	5664	5660	v st
0 3 1	6253	6245	v st
0 4 0	8589	8587	w
1 0 2	9507	9506	st
1 3 1	10096	10091	st
1 4 0	12439	12433	v w
0 4 2	14246	14247	st
0 5 1	14834	14832	w
2 0 0	15392	15386	st
0 3 3	17571	17565	st
1 4 2	18090	18093	m
1 5 1	18684	18678	w
0 6 0	19324	19320	m
2 0 2	21047	21046	m
1 3 3	21414	21412	st
2 3 1	21634	21631	st
0 0 4	22642	22640	m
1 6 0	23170	23167	m
0 6 2	24980	24980	m
0 5 3	26164	26152	v w
1 0 4	26488	26486	m
0 7 1	27711	27712	m
1 6 2	28827	28827	m
2 4 2	29631	29633	m
2 5 1	30206	30218	w
0 4 4	31223	31227	w
1 7 1	31558	31559	m
2 3 3	32943	32952	st
3 0 0	34628	34620	v w
2 6 0	34699	34707	m
1 4 4	35067	35073	w

sions, the possible space groups, and the appearance of the powder pattern indicate that the compound is of the U₃O₈ structure type.

The change in volume accompanying the phase transformation is -14%. A structural study of the phase is in progress.

The present study suggests that application of pressure to mixtures of NbO₂F-Nb₂O₅ results in a series of phases having distinctly different structure types, which are related to the series of compounds observed in the system Ta₂O₅-TaO₂F. Further investigations are contemplated. The high pressure chemistry of the niobium oxides has been discussed elsewhere.^{10,11}

Acknowledgements. The financial support of this work by the Swedish Natural Science Research Council is gratefully acknowledged.

1. Andersson, S. *Acta Chem. Scand.* **18** (1964) 2339.
2. Åström, A. *Acta Chem. Scand.* **20** (1966) 969.
3. Gruehn, R. *Naturwiss.* **54** (1967) 645.
4. Holmberg, B. *Private communication.*
5. Jahnberg, L. and Andersson, S. *Acta Chem. Scand.* **21** (1967) 615.
6. Lundberg, M. *Acta Chem. Scand.* **19** (1965) 2274.
7. Loopstra, B. O. *Acta Cryst.* **17** (1964) 651.
8. Frével, L. K. and Rinn, H. W. *Acta Cryst.* **9** (1956) 626.
9. Wilhelmi, K.-A. and Burger, W. *Acta Chem. Scand.* **23** (1969) 414.
10. Andersson, S. and Galy, J. J. *Solid State Chem.* **1** (1970) 576.
11. Wadsley, A. D. and Andersson, S. In *Perspectives in Structural Chemistry*, Vol. III, Wiley, New York (1970). *In print.*

Received April 30, 1970.

On the Crystal Structure of V₃O₇

STEN ANDERSSON

*Institute of Technology, Chemical Centre,
Department of Inorganic Chemistry,
Box 740, S-220 07 Lund 7, Sweden*

JEAN GALY

*Service de Chimie Minérale de la Faculté
des Sciences de Bordeaux, 33-Talence,
France*

KARL-AXEL WILHELMI

*University of Stockholm, Institute of
Inorganic and Physical Chemistry, Box 6801,
S-113 86 Stockholm, Sweden*

A new vanadium oxide, V₃O₇, was reported by Tudo and Tridot¹ to be formed when mixtures of V₂O₃ and V₂O₅ were heated in sealed silica tubes at 600°C. Crystals of the same compound can be made in supercritical water² and from this material single crystal data were collected with CuK radiation, using ordinary film technique and an integrating Nonius Weis-

senberg camera. Intensities were read visually. The unit cell dimensions, calculated from a powder pattern, obtained with a Hägg-Guinier camera, agree well with those reported by Thomas, Tudo and Tridot:¹

$$a = 21.92 \text{ \AA}; \quad b = 3.68 \text{ \AA}; \quad c = 18.34 \text{ \AA}; \\ \beta = 95.62^\circ$$

The observed density, 3.61 g/cm³, indicates a cell content of 12 formula units of V₃O₅ (calc. 12.1).

The probable space groups are *C2/c* and *Cc*. With the assumption that the vanadium atoms were five- as well as six-coordinated, several models for the structure were derived. The approximate vanadium positions of each model were refined with the Patterson projection *P(upv)*. With electron density calculations it was possible to exclude all the models except one, which refined to an *R* factor of 15 %, using the *h0l* data. The derived structure was now refined in *C2/c* with one vanadium and one oxygen in 4(*e*), four vanadium and ten oxygen atoms in 8(*f*), using 540 *h0l*, *h1l* and *h2l* reflections with a full-matrix least-squares program.⁴ At the present stage of refinement the *R* factor is 9.0 %.

In structures of this kind, with a short axis of 3.7 Å, atoms often lie within, or very close to two planes *b*/2 apart. In the structure of V₃O₅, certain atoms are slightly displaced from these two planes. The standard deviations in the *y* parameters obtained for these atoms are at present rather large. Further refinement is contemplated to obtain accurate bond distances. A complete three-dimensional set of intensities is being collected. Atomic positions and interatomic distances will be published later.

A schematic representation of the structure is given in Fig. 1. It is seen that octahedra, trigonal bipyramids, and square pyramids are the basic structural elements.

The unit cell of V₃O₅ contains thirty-six vanadium atoms. Twelve vanadium atoms are inside octahedra and twenty-four are in trigonal bipyramids (or square pyramids), see Fig. 1. This arrangement is in accordance with the assumption that the V⁴⁺ atoms are located in octahedra, whereas the V⁵⁺ atoms are inside polyhedra of five-fold coordination.

It is interesting to compare this structure with the so-called *S* units, used by Wads-

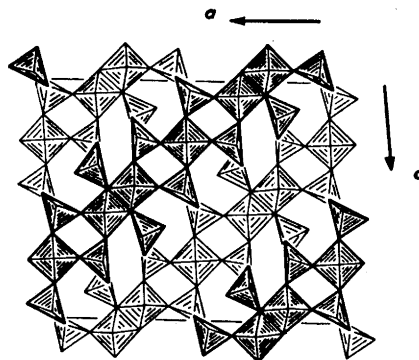


Fig. 1. The crystal structure of V₃O₅, projected on (010).

ley⁵ to describe the structures of TiNb₃O₇ and Ti₂Nb₁₀O₃₃. Here three octahedra are joined together by cornersharing, forming a row. Each such row is joined to two other rows by edgesharing, thus forming an *S* unit. The Nb₃O₇F structure⁶ represents a three-dimensional framework of such *S* units. The V₃O₅ structure can be described in terms of modified *S* units, in which two out of three octahedra have been transformed into trigonal bipyramids or square pyramids. The structure of V₃O₅ consists of modified *S* units that are joined together by cornersharing.

Acknowledgements. This investigation has been financed through a research grant from the Swedish Natural Science Research Council.

1. Tudo, J. and Tridot, G. *Compt. Rend.* **261** (1965) 2911.
2. Andersson, S. *Arkiv Kemi* **26** (1967) 521.
3. Thomas, D., Tudo, J. and Tridot, G. *Compt. Rend.* **265** (1967) 183.
4. Stewart, J. M. and High, D. *Crystal Structure Calculations System*, X-ray 63, TR-64-6 (NS 6-398), Computer Science Center, Univ. of Maryland and Research Computer Laboratory, Univ. of Washington.
5. Wadsley, A. D. *Acta Cryst.* **14** (1961) 660, 664.
6. Andersson, S. *Acta Chem. Scand.* **18** (1964) 2339.

Received April 30, 1970.