

## References

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS, A Fortran Crystallographic Least-Squares Program*. Report ORNL-TM-305. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- CONARD, B. R. (1969). Ph.D. thesis, Iowa State University.
- CONARD, B. R. & FRANZEN, H. F. (1971). *High Temp. Sci.* **3**, 49.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891.
- DAHM, D. J., BENSON, J. E., NIMROD, D. M., FITZWATER, D. R. & JACOBSON, R. A. (1967). USAEC Report IS-1701.
- EDSHAMMAR, L. E. (1962). *Acta Chem. Scand.* **16**, 20.
- FRANK, H. F. & KASPER, J. C. (1958). *Acta Cryst.* **11**, 184.
- FRANK, H. F. & KASPER, J. C. (1959). *Acta Cryst.* **12**, 483.
- FRANZEN, H. F. (1966). *J. Inorg. Nucl. Chem.* **28**, 1575.
- FRANZEN, H. F., BEINEKE, T. A. & CONARD, B. R. (1968). *Acta Cryst.* **B24**, 412.
- FRANZEN, H. F. & SMEGGIL, J. (1969). *Acta Cryst.* **B25**, 1736.
- FRANZEN, H. F. & SMEGGIL, J. (1970). *Acta Cryst.* **B26**, 125.
- FRANZEN, H. F., SMEGGIL, J. & CONARD, B. R. (1967). *Mat. Res. Bull.* **2**, 1087.
- HANSEN, H. P., HERMAN, F., LEA, J. D. & SKILLMAN, S. (1964). *Acta Cryst.* **17**, 1040.
- JAMIESON, J. C. (1963). *Science*, **140**, 72.
- OWENS, J. P., CONARD, B. R. & FRANZEN, H. F. (1967). *Acta Cryst.* **23**, 77.
- PEARSON, W. B. (1967). *A Handbook of Lattice Spacings and Structures of Metals and Alloys*, Vol. 2. International Series of Monographs in Metal Physics and Physical Metallurgy, Vol. 8. Oxford; Pergamon Press.
- PEDERSEN, B. & GRØNVOLD, F. (1959). *Acta Cryst.* **12**, 1022.
- SCHUBERT, K., RAMAN, A. & ROSSTEUTSCHER, W. (1964). *Naturwiss.* **51**, 506.

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## The Crystal Structure of $V_4O_7$

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Single crystals of  $V_4O_7$  were synthesized by the chemical transport method. They are triclinic with space group  $P\bar{1}$  and with  $a = 5.504$ ,  $b = 7.007$ ,  $c = 19.243$  Å,  $\alpha = 41.3$ ,  $\beta = 72.5$ ,  $\gamma = 109.4^\circ$  and  $Z = 2$ . 542 crystallographically independent reflexions were collected with a 4-circle single-crystal diffractometer. The structure was refined by full-matrix least-squares analysis to an  $R$  value of 0.084 for all the observed reflexions. The structure of  $V_4O_7$  indicates considerable displacements of atoms from the ideal structure proposed by Andersson & Jahnberg [*Ark. Kem.* (1963), **21**, 413]. In particular, the distortions of the  $VO_6$  octahedra in the crystallographic shear boundary are remarkable. The V–O distances are in the range  $1.78 \approx 2.12$  Å and the O–O distances in the range  $2.52 \approx 3.00$  Å. The shortest V–V distance is  $2.778$  Å in the crystallographic shear plane.

### Introduction

In the composition range  $VO_x$ ,  $1.750 < x < 1.887$ , the existence of the homologous series of  $V_nO_{2n-1}$  ( $4 \leq n \leq 8$ ), was<sup>‡</sup> revealed by X-ray powder diffraction (Andersson, Collen, Kuylenstierna & Magneli, 1957). The structure of  $Ti_5O_9$ , which is isostructural with  $V_5O_9$ , was then determined by the X-ray single-crystal method (Andersson, 1960). The structure model of  $Ti_5O_9$  was extended and successfully used to interpret the X-ray powder patterns of the other members

of the series of  $V_nO_{2n-1}$  and  $Ti_nO_{2n-1}$  by Andersson & Jahnberg (1963).

However, details of the crystal structures of the homologous series of  $V_nO_{2n-1}$  and  $Ti_nO_{2n-1}$  have been unknown because of the difficulty in obtaining single crystals suitable for X-ray single crystal work.

Single crystals of  $V_nO_{2n-1}$  ( $3 \leq n \leq 8$ ), of size 1 to 5 mm, were recently synthesized by the chemical transport method (Nagasawa, 1972), and the crystallography of  $V_nO_{2n-1}$  was studied, using these crystals, by the X-ray single-crystal method (Horiuchi, Tokonami, Morimoto, Nagasawa, Bando & Takada, 1972). According to this study, the lattices of the homologous series of  $V_nO_{2n-1}$  ( $a_n$ ,  $b_n$  and  $c_n$ ,  $4 \leq n \leq 8$ ) can be systematically described on the basis of the parent rutile-type lattice ( $a$ ,  $b$ , and  $c$ ), as follows:

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$$\begin{aligned} \mathbf{a}_n &= -\mathbf{a}_r + \mathbf{c}_r \\ \mathbf{b}_n &= \mathbf{a}_r + \mathbf{b}_r + \mathbf{c}_r \\ \mathbf{c}_n &= \frac{1}{2}(2n-1)(\mathbf{b}_r + \mathbf{c}_r). \end{aligned}$$

In this investigation the crystal structure of  $V_4O_7$  has been precisely determined in order to elucidate the deviation from the ideal structure derived from the parent rutile structure by introducing a crystallographic shear (Andersson & Jahnberg, 1963), and, especially to study the distortion of the  $VO_6$  octahedra in the crystallographic shear planes. The differences among the structures of the members of the homologous series must also be of interest in considering their crystal chemical characteristics. The details of the crystal structures of other members of the series will be published soon.

### Experimental

The single crystals of  $V_4O_7$  of size 1 to 5 mm were obtained by the chemical transport method (Nagasawa, 1972). As indicated by Andersson & Jahnberg (1963), the space group of  $V_4O_7$  was proved to be  $P1$  or  $P\bar{1}$  from the precession photographs. A small crystal fragment of size approximately  $0.03 \times 0.05 \times 0.03$  mm was used for collecting the three-dimensional intensity data, and 542 independent reflexions with  $2\theta \leq 45.0^\circ$  were measured with a RIGAKU four-circle automatic diffractometer using the  $2\theta$ - $\omega$  scan technique and Zr-filtered  $Mo K\alpha$  radiation ( $\lambda = 0.71069$  Å). The scanning width  $\Delta\omega$  was given by the relation;  $\Delta\omega = 0.60 + 0.30 \tan \theta$  (degrees). The integrated intensities were converted into structure factors by applying the Lorentz-polarization corrections. Absorption corrections were ignored owing to the small diameter of the specimen ( $\mu R = 0.26$ ).

The crystal lattice of  $V_4O_7$  was determined in accordance with the studies of Horiuchi *et al.* (1972), and the cell dimensions were obtained based upon the three high Bragg-angle reflexions,  $5\bar{2}0$ ,  $0\bar{2}0$  and  $1,6,18$  measured with the four-circle diffractometer. They are  $a = 5.504 \pm 0.003$ ,  $b = 7.007 \pm 0.004$ ,  $c = 10.243 \pm 0.009$  Å,  $\alpha = 41.3 \pm 0.1$ ,  $\beta = 72.5 \pm 0.1$  and  $\gamma = 109.4 \pm 0.1^\circ$ . These values are in good agreement with those obtained by Andersson & Jahnberg (1963), if their crystal axes are transformed by the matrix  $100/010/1\frac{1}{2}\frac{1}{2}$  (Horiuchi *et al.*, 1972). The standard deviations of the cell dimensions were estimated from the equation  $\Delta d/d = -\cot \theta \Delta\theta$ , where the above three Bragg angles were substituted for  $\theta$  and accuracy of the angles on the 4-circle diffractometer,  $1^\circ/100$  or  $1.7 \times 10^{-4}$  radians for  $\Delta\theta$ .

### Structure refinement

The refinement of the structure was initiated from the ideal structure given by Andersson & Jahnberg (1963). The initial atomic coordinates  $x$ ,  $y$  and  $z$  (Table 1) were obtained from those by Andersson & Jahnberg,

by the following relation (Horiuchi *et al.*, 1971),

$$\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} 1 & 0 & 4 \\ 0 & 1 & 5 \\ 0 & 0 & 2 \end{pmatrix} \begin{pmatrix} x_A \\ y_A \\ z_A \end{pmatrix} + \begin{pmatrix} \frac{1}{2} \\ 0 \\ \frac{1}{2} \end{pmatrix}.$$

Table 1. *The starting atomic coordinates and temperature factors for  $V_4O_7$*

These atomic coordinates are derived from the structure by Andersson & Jahnberg (1963) as explained in the text.

	$x$	$y$	$z$	$B$
V(1)	0	0.5	0.072	0.3
V(2)	0	0	0.072	0.3
V(3)	0	0.5	0.358	0.3
V(4)	0	0	0.358	0.3
O(1)	0.695	0.5	0.016	0.5
O(2)	0.306	0.614	0.094	0.5
O(3)	0.695	0.5	0.158	0.5
O(4)	0.306	0.5	0.270	0.5
O(5)	0.695	0.387	0.334	0.5
O(6)	0.306	0.613	0.380	0.5
O(7)	0.695	0.5	0.444	0.5

Full-matrix least-squares refinement was carried out using a FACOM 230-C0 version\* of the program *ORFLS* of Busing, Martin & Levy (1962). The function minimized in this refinement was  $\sum 1/\sigma_{hkl}^2 |sF_o - F_c|^2$ , where  $\sigma_{hkl}$  is the value given by the counting statistics when  $|F_o| \neq 0$ , and is 10.0 when  $|F_o| = 0$ , and  $s$  is the scale factor. Only the final refinement was carried out using equal weight for all reflexions as described later.

Atomic scattering factors used first for the vanadium and oxygen atoms were those of  $V^{3+}$  and  $O^{2-}$  respectively. However, as mentioned later, those of  $V^{3+}$  and  $V^{4+}$  for vanadium atoms were used in the last stage of the refinement in order to keep electrostatic neutrality. The atomic scattering factors for  $V^{3+}$  and  $V^{4+}$ , and for  $O^{2-}$  were taken from Fukamachi (1971) and Tokonami (1965) respectively. The isotropic temperature fac-

Table 2. *The final atomic coordinates and temperature factors for  $V_4O_7$*

Standard errors in parentheses apply to the last digits.

	$x$	$y$	$z$	$B$
V(1)	-0.00698 (97)	0.4482 (11)	0.09478 (40)	0.45 (4)
V(2)	-0.01739 (95)	-0.0610 (11)	0.10066 (39)	0.34 (4)
V(3)	-0.01163 (96)	0.4870 (11)	0.36698 (40)	0.43 (4)
V(4)	-0.03145 (95)	-0.0363 (11)	0.37327 (40)	0.37 (4)
O(1)	0.6973 (40)	0.4174 (46)	0.0498 (16)	1.04 (19)
O(2)	0.3230 (40)	0.5560 (46)	0.1039 (16)	0.98 (18)
O(3)	0.6896 (39)	0.4735 (45)	0.1684 (16)	0.78 (17)
O(4)	0.3829 (38)	0.6268 (44)	0.2235 (16)	0.71 (17)
O(5)	0.6934 (39)	0.4161 (45)	0.3317 (16)	1.01 (18)
O(6)	0.3026 (40)	0.5661 (46)	0.3924 (16)	1.05 (18)
O(7)	0.6602 (38)	0.4332 (43)	0.4697 (16)	0.67 (17)

\* The least-squares program for the FACOM 230-60 was modified by Syoyama and Horiuchi from the program *RSFLS4* (HITAC 5020E version of *ORFLS*) of the UNICS system. (Saturai, 1967).

tors were initially assumed to be  $0.3 \text{ \AA}^2$  for vanadium atoms and  $0.5 \text{ \AA}^2$  for oxygen atoms.

The initial structure mentioned above gave  $R(\sum |F_o| - |F_c|) / \sum |F_o| = 0.493$  for all 542 reflexions. The first four cycles of least-squares on  $F_o$ 's were carried out varying only the atomic coordinates and the scale factor and the  $R$  value dropped to 0.098. In the next two cycles, the isotropic temperature factors were allowed to vary. The atomic coordinates and the isotropic temperature factors were refined at the same time in the next five cycles, which reduced the  $R$  value

to 0.093 and the weighted  $R$  value to 0.077 for all reflexions. Finally, the atomic coordinates and the isotropic temperature factors were refined using equal weight for all reflexions. This reduced the  $R$  value to 0.084 for all reflexions and 0.069 for all non-zero reflexions.

In order to examine the possibility of space group  $P1$ , a three-dimensional  $F_o - F_c$  synthesis was calculated with the final atomic coordinates and temperature factors by using the FACOM 230-60 version of the program 3DFR written by Iitaka and Matsusaki.

Table 3. Observed and calculated structure factors for  $V_4O_7$ .

The three columns are, in order:  $l$ ,  $10|F_o|$ ,  $10F_c$ .

h=0, k=0		h=1, k=0		h=2, k=1		h=3, k=1		h=-1, k=2		h=-2, k=2		h=-3, k=2		h=-4, k=3			
-1	128	150	2	210	190	12	0	-14	8	60	-69	7	1141	-1244	7	457	-466
-2	211	215	1	248	258	11	95	-87	7	521	-547	6	342	-328	6	306	-314
-3	233	208	0	919	921	10	78	-91				5	210	-197	5	135	-145
-4	926	-954	-1	0	-23	9	32	12				4	876	-858	4	703	-721
-5	170	-166	-2	149	158	8	79	-60	18	66	-71	3	994	918	3	640	653
-6	223	-218	-3	165	150	7	602	610	16	56	24	2	439	409	2	408	399
			-4	618	-644	6	52	50	15	0	18	1	275	275	1	225	215
9	0	-31				5	42	-51	14	312	287	0	1148	1197	0	494	418
8	0	42	11	69	28	4	37	-18	13	0	-4	-1	211	-220	-1	193	-187
7	74	-33	10	0	45	3	56	75	12	58	84	-2	85	-78	-2	139	-141
6	23	-1	9	52	-27	2	0	-11	11	0	-34				-3	5	39
5	33	16	8	22	-4										-4	664	-676
4	23	2	7	611	-583	15	529	-504									
3	26	26	6	0	-11	14	441	409	19	58	25						
2	43	-29	5	47	-34	13	213	201	18	664	-658	9	44	32	9	17	14
1	68	67	4	0	5	12	227	206	8	50	57	8	67	14	7	88	56
0	661	-664	3	69	50	11	1107	1135	7	579	574	7	88	56	6	52	-29
-1	73	-84	2	60	-62	10	59	-53	5	0	-39	5	0	-7	0	0	-7
-2	0	-9	1	8	3	9	69	58	4	60	-52	4	119	117	-1	22	-39
-3	0	-0	0	245	235	8	103	108	3	42	-50	3	58	-45	-2	33	24
			-1	0	-21	7	1265	-1346	8	249	249	2	0	-24	9	163	-161
						6	153	-158	7	367	-378	1	89	78	8	64	76
						5	242	-238	6	89	-88	0	314	312	7	479	-494
									5	290	-289	-1	0	-21	6	234	-226
															5	0	2
															4	389	-351
															3	701	684
															2	335	317
															1	139	129
															8	0	-7
															7	1216	-1318
															6	129	-133
															5	0	10
															4	355	-337
															3	803	806
															2	236	227
															6	24	8
															5	35	-23
															4	125	97
															13	37	19
															12	65	29
															11	0	39
															10	0	-2
															9	61	49
															8	44	-39
															7	333	294
															6	75	43
															5	40	-42
															4	536	-513
															3	0	-3
															2	73	49
															1	29	-29
															10	0	33
															11	400	384
															10	532	-503
															9	289	-281
															8	115	-106
															-11	657	671
															-12	76	-14
															-13	36	-63
															15	0	-10
															14	51	33
															13	69	-61
															12	62	31
															-4	119	117
															-5	7	-24
															-6	0	14
															-7	355	-323
															-8	0	8
															-9	40	3
															-10	71	85
															1	51	67
															0	694	866
															-1	0	-6
															-2	154	-152
															-3	224	214
															-4	972	-1005
															-5	0	9
															-6	124	-99
															-7	205	-195
															-8	0	5

This gave zero electron density in the whole unit cell, which confirmed that the space group was  $P\bar{1}$ .

The final atomic coordinates and the temperature factors are given in Table 2. Observed and calculated structure factors are compared in Table 3.

### Discussion of the structure

The structure of  $V_4O_7$  obtained in this investigation is schematically shown on the basis of the rutile-type lattice,  $a_r$ ,  $b_r$  and  $c_r$  ( $r$  represents the rutile-type cell,

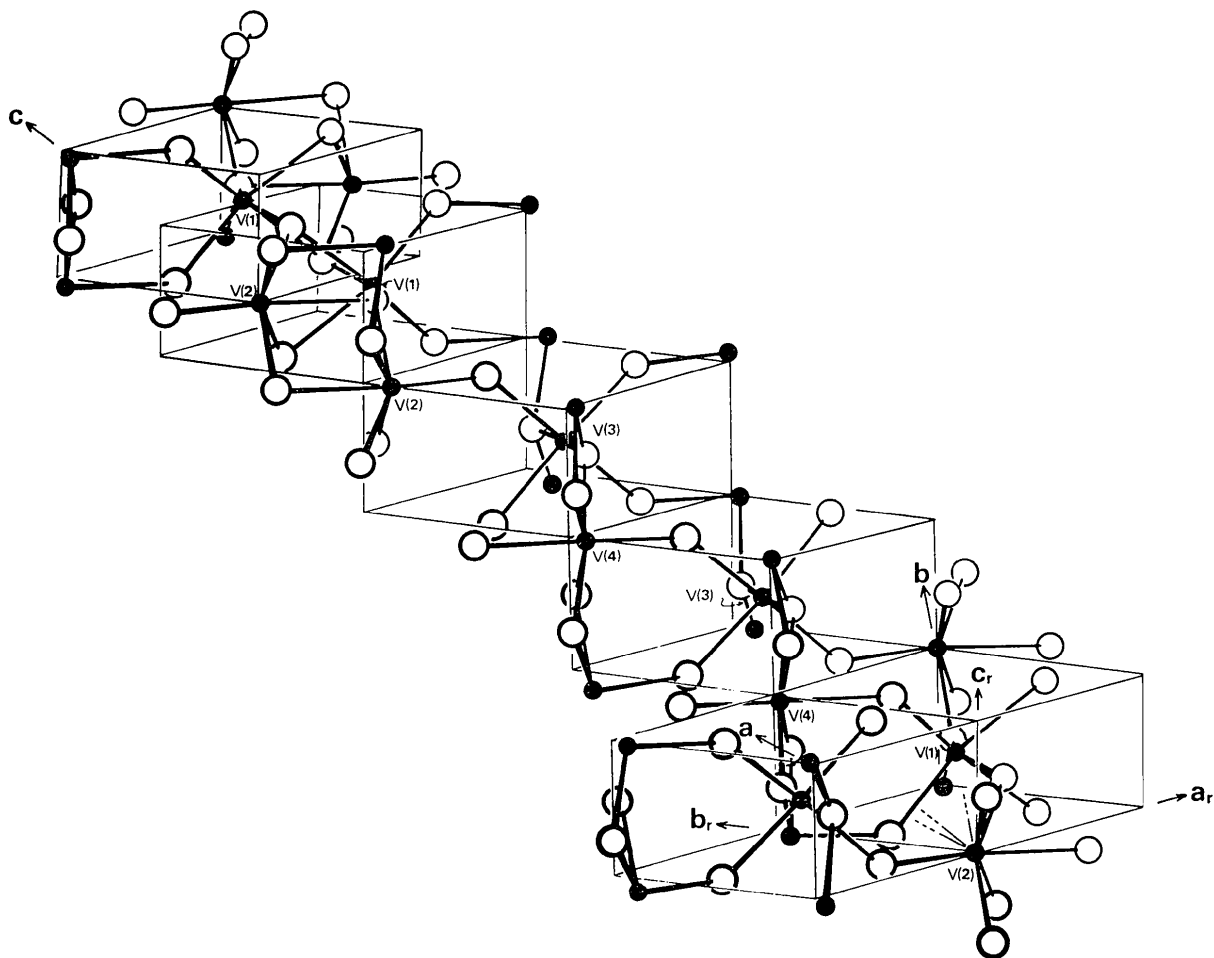


Fig. 1. The crystal structure of  $V_4O_7$ . The lattice vectors of  $V_4O_7$  are shown by  $a$ ,  $b$ , and  $c$ . Tetragonal rutile-type lattices ( $a_r$ ,  $b_r$  and  $c_r$ ) are shown with fine lines.

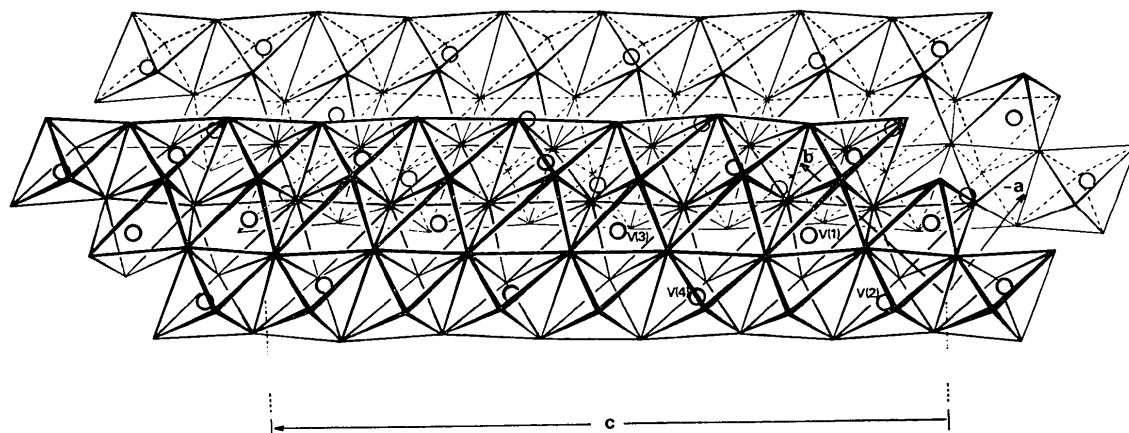


Fig. 2. The arrangement of the octahedra of oxygen atoms in the structure of  $V_4O_7$ . Open circles represent vanadium atoms.

Fig. 1). Interatomic distances and bond angles (Table 4) were calculated by using the FACOM 230-60 version of the program *RDA4* of the UNICS system (Sakurai, 1967).

According to Andersson & Jahnberg (1963), the structure of  $V_nO_{2n-1}$  and  $Ti_nO_{2n-1}$  can be described as follows: their structures are built up of slabs of a rutile-type structure, the slabs being of infinite extension in two dimensions, and mutually connected along the 'crystallographic shear plane' (Wadsley, 1955) by  $VO_6$  octahedra which share faces in the fashion of the corundum-type structures.

The structure of  $V_4O_7$  confirms their general description of the structures of  $V_nO_{2n-1}$ . The arrangement of oxygen atoms is in deformed hexagonal close packing and is similar to the arrangement of the oxygen atoms in the rutile-type structure. The arrangement of the octahedra of oxygen atoms in  $V_4O_7$  is shown in Fig. 2. Because the crystallographic shear plane is parallel to  $(001)$ , or  $(\bar{1}\bar{2}1)_r$ , and the displacement of the adjacent rutile-type slabs is  $\frac{1}{2}[001]$ , or  $\frac{1}{2}[011]_r$ , the oxygen lattices are continuous but the vanadium lattices are in antiphase relation across the shear plane. The structure of  $V_4O_7$  is, therefore, considered to consist of two portions: rutile-type and corundum-type.

Two octahedra of V(1) and V(2) constitute the crys-

tallographic shear plane of the corundum-type structure (Fig. 3) and the other two octahedra of V(3) and V(4) the rutile-type slabs (Fig. 4). The deviations of the atomic coordinates from those in the ideal structure derived by Andersson & Jahnberg are not much for most atoms, but those of O(4) amount to 0.42, 0.89 and 0.90 Å along  $a$ ,  $b$  and  $c$  axes respectively. The results of this investigation reveal that the portion of the corundum-type structure in  $V_4O_7$  resembles more closely the real corundum structure than the ideal structure of Andersson & Jahnberg suggests.

Because of this result and electrostatic neutrality, atomic scattering factors for  $V^{3+}$  and  $V^{4+}$  were used in the final stage of the structure analysis for the vanadium atoms in the corundum-type portions [V(1) and V(2)] and in the rutile-type portions [V(3) and V(4)] respectively, though the conclusion about the valency of the vanadium atoms has not been confirmed by this structure refinement. Temperature factors (Table 2) for all atoms are nearly consistent with other oxides: isotropic values for vanadium atoms are in the range, 0.34 to 0.45 Å<sup>2</sup>, and for oxygen atoms in the range, 0.67 to 1.05 Å<sup>2</sup>.

In the portion which has the corundum-type structure (Fig. 3), metal atoms shift away from the centres of the oxygen octahedra so as to become further apart because of sharing of the octahedral faces. However,

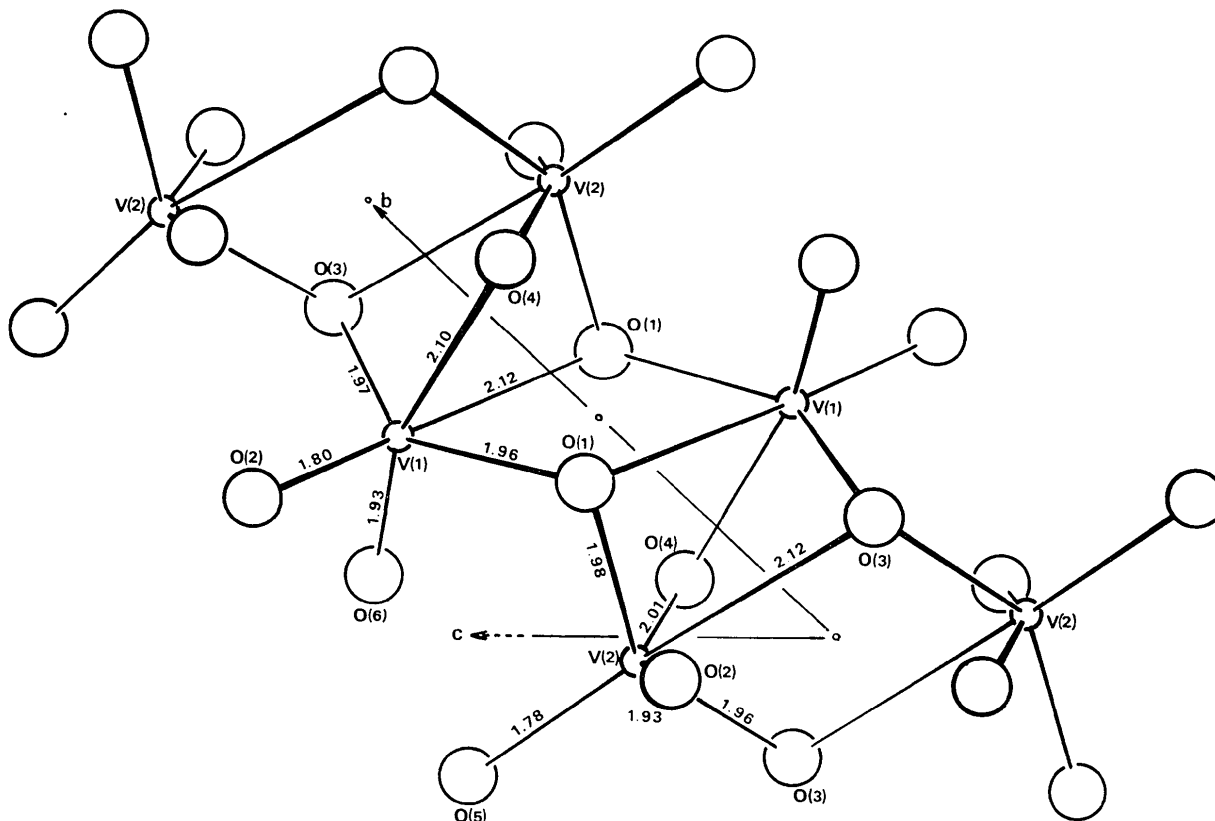


Fig. 3. Perspective view of the portion of the structure of  $V_4O_7$  showing the corundum-type structure. Bond lengths (Å) are given.

Table 4. Bond distances (Å) and angles (°)

Symmetry codes are given below.  
(I) Bond distances. Standard errors in parentheses apply to the last digits.

V(1)-O octahedron	V(1)-O(1) <i>a</i>	2.12 (3)	O(1) <i>a</i> -O(1) <i>f</i>	2.53 (4)
	V(1)-O(1) <i>f</i>	1.96 (4)	O(1) <i>a</i> -O(3) <i>a</i>	2.58 (6)
	V(1)-O(2)	1.80 (3)	O(1) <i>a</i> -O(4) <i>g</i>	2.62 (3)
	V(1)-O(3) <i>a</i>	1.97 (4)	O(1) <i>a</i> -O(6) <i>c</i>	2.75 (3)
	V(1)-O(4) <i>g</i>	2.10 (1)	O(1) <i>f</i> -O(2)	2.86 (6)
	V(1)-O(6) <i>c</i>	1.93 (1)	O(1) <i>f</i> -O(4) <i>g</i>	2.69 (5)
	Average	1.98	O(1) <i>f</i> -O(6) <i>c</i>	2.90 (3)
			O(2)-O(3) <i>a</i>	3.00 (4)
			O(2)-O(4) <i>g</i>	2.95 (3)
			O(2)-O(6) <i>c</i>	2.87 (3)
			O(3) <i>a</i> -O(4) <i>g</i>	2.63 (3)
			O(3) <i>a</i> -O(6) <i>c</i>	2.82 (4)
			Average	2.77
	V(2)-O octahedron	V(2)-O(1) <i>f</i>	1.98 (3)	O(1) <i>f</i> -O(2) <i>f</i>
V(2)-O(2) <i>f</i>		1.93 (2)	O(1) <i>f</i> -O(3) <i>f</i>	2.58 (6)
V(2)-O(3) <i>c</i>		1.96 (4)	O(1) <i>f</i> -O(4) <i>f</i>	2.62 (3)
V(2)-O(3) <i>f</i>		2.12 (3)	O(1) <i>f</i> -O(5) <i>c</i>	2.99 (3)
V(2)-O(4) <i>c</i>		2.01 (2)	O(2) <i>f</i> -O(3) <i>c</i>	2.87 (3)
V(2)-O(5) <i>d</i>		1.78 (3)	O(2) <i>f</i> -O(3) <i>f</i>	2.67 (4)
Average		1.96	O(2) <i>f</i> -O(5) <i>c</i>	2.79 (3)
			O(3) <i>c</i> -O(3) <i>f</i>	2.52 (3)
			O(3) <i>c</i> -O(4) <i>c</i>	2.64 (5)
			O(3) <i>c</i> -O(5) <i>c</i>	2.86 (5)
			O(3) <i>f</i> -O(4) <i>c</i>	2.63 (3)
			O(4) <i>c</i> -O(5) <i>c</i>	2.94 (4)
			Average	2.74
V(3)-O octahedron		V(3)-O(1) <i>b</i>	2.03 (1)	O(1)-O(4)
	V(3)-O(4)	2.06 (4)	O(1) <i>b</i> -O(5) <i>a</i>	2.91 (3)
	V(3)-O(5) <i>a</i>	2.00 (3)	O(1) <i>b</i> -O(6)	2.75 (3)
	V(3)-O(5) <i>i</i>	1.98 (1)	O(1) <i>b</i> -O(7) <i>a</i>	2.84 (3)
	V(3)-O(6)	1.95 (3)	O(4)-O(5) <i>a</i>	2.08 (4)
	V(3)-O(7) <i>a</i>	1.90 (4)	O(4)-O(5) <i>i</i>	2.97 (3)
	Average	1.99	O(4)-O(6)	2.81 (6)
			O(5) <i>a</i> -O(5) <i>i</i>	2.70 (3)
			O(5) <i>a</i> -O(7)	2.70 (6)
			O(5) <i>i</i> -O(6)	2.89 (3)
			O(5) <i>i</i> -O(7) <i>a</i>	2.75 (5)
			O(6)-O(7) <i>a</i>	2.86 (4)
			Average	2.81
	V(4)-O octahedron	V(4)-O(2)	2.04 (2)	O(2)-O(3)
V(4)-O(3)		2.04 (2)	O(2)-O(4)	2.78 (6)
V(4)-O(4)		2.01 (3)	O(2)-O(7) <i>c</i>	2.69 (3)
V(4)-O(6) <i>i</i>		1.87 (3)	O(2)-O(7) <i>i</i>	2.79 (3)
V(4)-O(7) <i>c</i>		1.93 (4)	O(3)-O(4)	2.64 (5)
V(4)-O(7) <i>i</i>		1.89 (2)	O(3)-O(6)	2.81 (3)
Average		1.96	O(3)-O(7) <i>c</i>	2.90 (3)
			O(4)-O(6) <i>i</i>	2.90 (3)
			O(4)-O(7) <i>i</i>	2.94 (3)
			O(6) <i>i</i> -O(7) <i>c</i>	2.73 (5)
			O(6) <i>i</i> -O(7) <i>i</i>	2.80 (4)
			O(7) <i>c</i> -O(7) <i>i</i>	2.61 (5)
			Average	2.77
V-V distances		V(1)-V(2) <i>e</i>	2.778 (9)	
	V(1)-V(3) <i>c</i>	2.930 (8)		
	V(1)-V(3) <i>g</i>	3.020 (7)		
	V(2)-V(4) <i>c</i>	2.964 (8)		
	V(2)-V(4) <i>f</i>	3.060 (7)		
	V(2)-V(2) <i>d</i>	3.20 (1)		

Table 4 (cont.)

(II) Bond angles,

V(1) octahedron	O(1) <i>a</i> -V(1)-O(1) <i>f</i>	76.5 ± 1.3		
	O(1) <i>a</i> -V(1)-O(3) <i>a</i>	78.2 ± 1.4		
	O(1) <i>a</i> -V(1)-O(4) <i>g</i>	76.9 ± 0.9		
	O(1) <i>a</i> -V(1)-O(6) <i>c</i>	85.3 ± 1.0		
	O(1) <i>f</i> -V(1)-O(2)	98.7 ± 1.5		
	O(1) <i>f</i> -V(1)-O(4) <i>g</i>	83.0 ± 1.2		
	O(1) <i>f</i> -V(1)-O(6) <i>c</i>	96.3 ± 1.3		
	O(2)-V(1)-O(3) <i>a</i>	105.5 ± 1.7		
	O(2)-V(1)-O(4) <i>g</i>	97.7 ± 0.9		
	O(2)-V(1)-O(6) <i>c</i>	100.3 ± 1.0		
	O(3) <i>a</i> -V(1)-O(4) <i>g</i>	80.5 ± 1.0		
	O(3) <i>a</i> -V(1)-O(6) <i>c</i>	92.6 ± 1.1		
	O(1) <i>a</i> -V(1)-O(2)	173.1 ± 0.8		
	O(1) <i>a</i> -V(1)-O(3) <i>a</i>	152.3 ± 1.2		
	O(1) <i>a</i> -V(1)-O(6) <i>c</i>	161.8 ± 1.2		
	V(2) octahedron	O(1) <i>f</i> -V(2)-O(2) <i>f</i>	91.2 ± 1.1	
		O(1) <i>f</i> -V(2)-O(3) <i>f</i>	78.1 ± 1.4	
		O(1) <i>f</i> -V(2)-O(4) <i>c</i>	82.3 ± 1.1	
		O(1) <i>f</i> -V(2)-O(5) <i>c</i>	105.6 ± 1.6	
		O(2) <i>f</i> -V(2)-O(3) <i>c</i>	95.1 ± 1.4	
O(2) <i>f</i> -V(2)-O(3) <i>f</i>		82.4 ± 1.0		
O(2) <i>f</i> -V(2)-O(5) <i>c</i>		97.4 ± 1.1		
O(3) <i>c</i> -V(2)-O(3) <i>f</i>		76.5 ± 1.2		
O(3) <i>c</i> -V(2)-O(4) <i>c</i>		83.3 ± 1.3		
O(3) <i>c</i> -V(2)-O(5) <i>c</i>		99.9 ± 1.3		
O(3) <i>f</i> -V(2)-O(4) <i>c</i>		79.0 ± 0.9		
O(4) <i>c</i> -V(2)-O(5) <i>c</i>		101.4 ± 1.0		
O(1) <i>f</i> -V(2)-O(3) <i>c</i>		152.7 ± 1.2		
O(2) <i>f</i> -V(2)-O(4) <i>c</i>		161.2 ± 1.0		
V(3) octahedron	O(3) <i>f</i> -V(2)-O(5) <i>c</i>	176.3 ± 1.7		
	O(1) <i>b</i> -V(3)-O(4)	82.4 ± 1.2		
	O(1) <i>b</i> -V(3)-O(5) <i>a</i>	92.3 ± 1.0		
	O(1) <i>b</i> -V(3)-O(6)	87.1 ± 0.9		
	O(1) <i>b</i> -V(3)-O(7) <i>a</i>	92.4 ± 1.2		
	O(4)-V(3)-O(5) <i>a</i>	87.5 ± 1.4		
	O(4)-V(3)-O(5) <i>i</i>	94.7 ± 1.2		
	O(4)-V(3)-O(6)	88.7 ± 1.4		
	O(5) <i>a</i> -V(3)-O(5) <i>i</i>	85.7 ± 1.0		
	O(5) <i>a</i> -V(3)-O(7) <i>a</i>	87.9 ± 1.4		
	O(5) <i>i</i> -V(3)-O(6)	94.7 ± 1.0		
	O(5) <i>i</i> -V(3)-O(7) <i>a</i>	90.3 ± 1.1		
	O(6)-V(3)-O(7) <i>a</i>	95.8 ± 1.5		
	O(1) <i>b</i> -V(3)-V(5) <i>i</i>	176.6 ± 1.8		
V(4) octahedron	O(4)-V(3)-O(7) <i>a</i>	172.9 ± 0.9		
	O(5) <i>a</i> -V(3)-O(6)	176.3 ± 1.6		
	O(2)-V(4)-O(3)	81.9 ± 1.0		
	O(2)-V(4)-O(3)	86.5 ± 1.3		
	O(2)-V(4)-O(7) <i>c</i>	85.1 ± 1.3		
	O(2)-V(4)-O(7) <i>i</i>	90.4 ± 1.0		
	O(3)-V(4)-O(4)	81.3 ± 1.2		
	O(3)-V(4)-O(6) <i>i</i>	91.7 ± 1.0		
	O(3)-V(4)-O(7) <i>c</i>	93.8 ± 1.3		
	O(4)-V(4)-O(6) <i>i</i>	96.4 ± 1.4		
	O(4)-V(4)-O(7) <i>i</i>	97.6 ± 1.3		
	O(6) <i>i</i> -V(4)-O(7) <i>c</i>	91.5 ± 1.4		
	O(6) <i>i</i> -V(4)-O(7) <i>i</i>	96.1 ± 1.0		
	O(7) <i>c</i> -V(4)-O(7) <i>i</i>	86.2 ± 1.3		
Symmetry codes	O(2)-V(4)-O(6) <i>i</i>	172.5 ± 1.4		
	O(3)-V(4)-O(7) <i>c</i>	172.2 ± 1.0		
	O(4)-V(4)-O(7) <i>c</i>	170.7 ± 1.0		
	none	<i>x</i>	<i>y</i>	<i>z</i>
	<i>a</i>	-1 + <i>x</i>	<i>y</i>	<i>z</i>
	<i>b</i>	<i>x</i>	1 + <i>y</i>	<i>z</i>
	<i>c</i>	-1 + <i>x</i>	-1 + <i>y</i>	<i>z</i>
<i>d</i>	- <i>x</i>	- <i>y</i>	- <i>z</i>	
<i>e</i>	- <i>x</i>	1 - <i>y</i>	- <i>z</i>	
<i>f</i>	1 - <i>x</i>	1 - <i>y</i>	- <i>z</i>	
<i>g</i>	1 - <i>x</i>	2 - <i>y</i>	- <i>z</i>	
<i>h</i>	2 - <i>x</i>	3 - <i>y</i>	- <i>z</i>	
<i>i</i>	- <i>x</i>	- <i>y</i>	1 - <i>z</i>	

the V(1)-V(2)*e* distance is still shortest in the structure at 2.77 Å. The oxygen octahedra display large deviations from the regular octahedron as shown by the interatomic distances and bond angles (Table 4). The V(1)-O<sub>6</sub> and V(2)-O<sub>6</sub> distances change widely from 1.80 to 2.12 Å and from 1.78 to 2.12 Å respectively. The bond angles of the type O-V(1)-O are in the range 76.5 to 105.5° and 152.3 to 173.1° and those of the type O-V(2)-O in the range 76.5 to 105.6° and 152.7 to

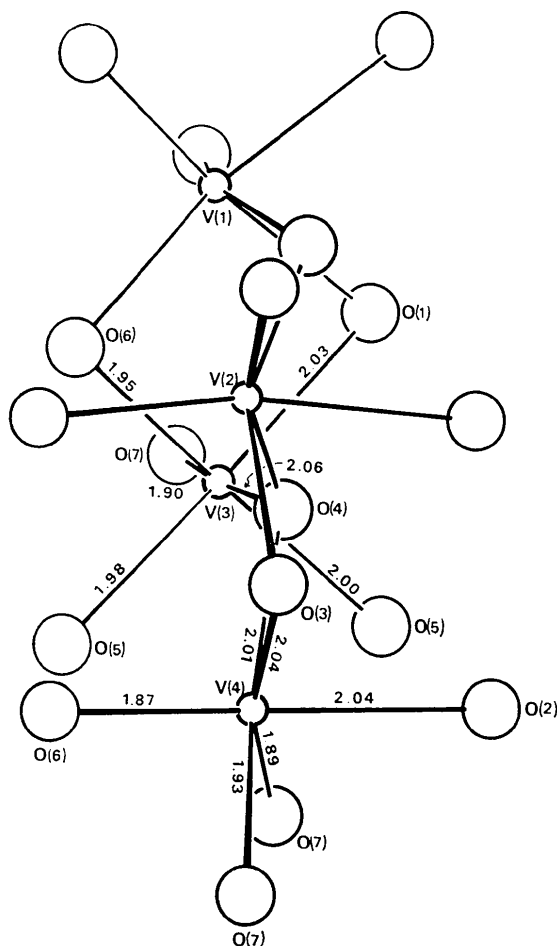


Fig. 4. Perspective view of the portion of the structure of  $V_4O_7$  showing the rutile-type structure. Bond lengths (Å) are given.

176.3°, compared with 90 and 180° in the regular octahedron.

In the portion which has the rutile-type structure (Fig. 4) the deviations of the oxygen octahedra from regularity are much less than those in the corundum-

type portion and vanadium atoms occupy positions almost at the centres of the octahedra. The interatomic distances of V(3)-O<sub>6</sub> and V(4)-O<sub>6</sub> are in the ranges 1.90 to 2.06 and 1.87 to 2.04 Å respectively; the bond angles of the type O-V(3)-O are in the range 82.4 to 95.8° and 172.9 to 176.6°, and those of the type O-V(4)-O, in the range 81.3 to 97.6° and 170.7 to 172.5°.

It is of interest to compare the structure of  $V_4O_7$  with those of  $V_2O_3$  (Newnham & Hann, 1962: V-O, 1.96 and 2.06 Å) and  $VO_2$  (Longo & Kierkegaard, 1970: V-O, 1.762 to 2.063 Å).  $V_2O_3$  has a corundum-type structure and  $VO_2$  a rutile-type structure above about 70°C. The metal atoms in corundum-type portions of the structure in  $V_4O_7$  show a greater deviation from the centres of the oxygen octahedra than those in  $V_2O_3$ . The portions of the rutile-type structure in  $V_4O_7$  are very similar to the structure of the high temperature form  $VO_2$ . A comparison with the structures of other  $V_nO_{2n-1}$  will be given soon.

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#### References

- ANDERSSON, S. (1960). *Acta Chem. Scand.* **14**, 1161.  
 ANDERSSON, S., COLLEN, B., KUYLENSTIERNA, U. & MAGNELI, A. (1957). *Acta Chem. Scand.* **11**, 1641.  
 ANDERSSON, S. & JAHNBERG, L. (1963). *Ark. Kem.* **21**, 413.  
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). Program *ORFLS*. Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee.  
 FUKAMACHI, T. (1971). *Tech. Rep. ISSP, B*, **12**, 1.  
 HORIUCHI, H., TOKONAMI, M., MORIMOTO, N., NAGASAWA, K., BANDO, Y. & TAKADA, T. (1972). *Mat. Res. Bull.* In the press.  
 LONGO, J. M. & KIERKEGAARD, P. (1970). *Acta Chem. Scand.* **24**, 420.  
 NAGASAWA, K. (1972). *Mat. Res. Bull.* In the press.  
 NEWNHAM, R. E. & DE HAAN, Y. M. (1962). *Z. Kristallogr.* **117**, 235.  
 SAKURAI, T. (1967). Universal Cryst. Comput. Prog. Sys. (UNICS). Tokyo: Cryst. Soc. of Japan.  
 TOKONAMI, M. (1965). *Acta Cryst.* **19**, 486.  
 WADSLAY, A. D. (1955). *Rev. Pure Appl. Chem.* **5**, 165.