

The Crystal Structure of V_3O_7

BY KJELL WALTERSSON, BERTIL FORSLUND AND KARL-AXEL WILHELMI

Department of Inorganic Chemistry, Arrhenius Laboratory, University of Stockholm, Fack, S-104 05 Stockholm, Sweden

STEN ANDERSSON

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

AND JEAN GALY

Service de Chimie Minérale de la Faculté des Sciences de Bordeaux, associé au CNRS, 351 cours de la Libération, 33-Talence, France

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The crystal structure of V_3O_7 has been determined from three-dimensional X-ray diffractometer data (Mo $K\alpha$ radiation). The monoclinic unit cell, space group $C2/c$ (No. 15), has the dimensions $a = 21.921$ (3), $b = 3.679$ (1), $c = 18.341$ (2) Å, and $\beta = 95.61^\circ$ (1); $V = 1472.1$ Å³. Least-squares refinement reached $R_w = 0.029$ for 1533 measured independent reflexions for which $\sigma(F_o)/|F_o| \leq 0.20$. The unit cell contains 12 formula units of V_3O_7 . 12 vanadium atoms have octahedral coordination of oxygen atoms, 16 are inside trigonal bipyramids and eight in square pyramids. The polyhedra are joined by corner- and edge-sharing to form a three-dimensional framework. The average V–O distances for the six- and five-coordinated metal atoms are 1.943 and 1.825 Å, respectively. Magnetic susceptibility measurements are in agreement with the formulation $V^{4+}V_2^{5+}O_7$.

Introduction

The atomic positions in the structure of V_6O_{13} were recently refined by Wilhelmi, Waltersson & Kihlberg (1971). The structure proposed by Aebi (1948) was confirmed.

The preparation of V_3O_7 , another intermediate in composition between V_2O_5 and VO_2 , was reported some years ago (Tudo & Tridot, 1965; Thomas, Tudo & Tridot, 1967). A preliminary note published by Andersson, Galy & Wilhelmi (1970) gave a structure derived from film data. The structure of the new oxide has now been refined, using single-crystal data collected with an automatic diffractometer.

Experimental

Preparation and determination of cell dimensions

The starting materials were divanadium pentoxide (p.a. LKB-Produkter, Stockholm, Sweden) and pure divanadium trioxide, obtained by reduction of V_2O_5 with hydrogen.

Polycrystalline samples of V_3O_7 were prepared from relatively large amounts (about 25 g) of V_2O_5 and V_2O_3 in sealed evacuated Vycor tubes at 550°C. After several heat treatments with intervening grindings the powder photographs of the final products contained only lines belonging to V_3O_7 (see below). Powder photographs of samples tempered above 600°C indicated that V_6O_{13} was also present in small amounts.

The powder photographs were taken with a Guinier-Hägg camera at 20°C, using Cu $K\alpha_1$ radiation and potassium chloride as internal standard ($a = 6.2930$ Å;

Table 1. Powder pattern of V_3O_7

Cu $K\alpha_1$ radiation ($\lambda = 1.54050$ Å).

<i>h</i>	<i>k</i>	<i>l</i>	d_{obs}	$10^5 \sin^2 \theta_{obs}$	$10^5 \sin^2 \theta_{calc}$	I_{obs}
2	0	0	10.89	500	499	<i>vvw</i>
4	0	0	5.451	1997	1994	<i>vvw</i>
0	0	4	4.557	2857	2849	<i>vw</i>
4	0	2	4.488	2945	2940	<i>w</i>
2	0	4	4.069	3584	3581	<i>m</i>
6	0	0	3.638	4484	4488	<i>m</i>
1	1	-1	3.568	4659	4657	<i>vs</i>
6	0	-2	3.499	4845	4850	<i>w</i>
0	0	6	3.042	6410	6410	<i>m</i>
2	0	-6	3.008	6555	6559	<i>m</i>
3	1	-3	2.945	6842	6846	<i>m</i>
2	0	6	2.859	7256	7259	<i>w</i>
3	1	3	2.837	7370	7371	<i>w</i>
6	0	4	2.716	8040	8036	<i>vvw</i>
5	1	-3	2.617	8663	8665	<i>vvw</i>
1	1	-5	2.595	8812	8814	<i>vw</i>
1	1	5	2.552	9108	9106	<i>s</i>
3	1	-5	2.496	9519	9520	<i>vvw</i>
6	0	-6	2.455	9845	9848	<i>m</i>
7	1	-1	2.3815	10461	10466	<i>vvw</i>
10	0	0	2.1823	12457	12465	<i>w</i>
8	0	-6	2.1364	12999	12989	<i>vvw</i>
1	1	7	2.1024	13423	13438	<i>vvw</i>
3	1	-7	2.0878	13611	13619	<i>vvw</i>
10	0	2	2.0750	13779	13761	<i>vvw</i>
6	0	-8	2.0232	14494	14485	<i>vvw</i>
7	1	5	1.9278	15964	15964	<i>vvw</i>
6	0	8	1.8528	17282	17283	<i>vw</i>
0	2	0	1.8398	17527	17535	<i>vs</i>
0	0	10	1.8251	17811	17807	<i>s</i>
4	0	-10	1.7837	18647	18635	<i>m</i>
12	0	2	1.7508	19354	19362	<i>vw</i>
4	2	2	1.7025	20468	20475	<i>vw</i>
5	1	-9	1.6967	20610	20612	<i>vw</i>
2	2	4	1.6757	21129	21116	<i>vw</i>
6	2	0	1.6412	22025	22023	<i>m</i>
6	2	-2	1.6280	22384	22385	<i>vvw</i>

Hambling, 1953). Refinement of the cell dimensions was performed by the method of least squares. The indexed powder pattern is listed in Table 1; the cell parameters are $a=21.921$ (3), $b=3.679$ (1), $c=18.341$ (2) Å and $\beta=95.61$ (1)°.

The density of the crystals, 3.61 g cm^{-3} , was determined from the loss of weight in benzene. This is in good agreement with a cell content of 12 V_3O_7 formula units in the cell ($d_{\text{calc}}=3.58 \text{ g cm}^{-3}$).

Portions of a well homogenized polycrystalline sample (1–2 mg) prepared at 550°C were analysed for oxygen according to a method described by Danielsson, Jonsson & Wilhelmi (1971). The oxygen content was found (mean value of ten runs) to be 42.26% (calculated value for $\text{V}_3\text{O}_7=42.290\%$).

Single crystals of V_3O_7 were prepared by treating mixtures (100–200 mg) of divanadium pentoxide and divanadium trioxide, having the gross composition $\text{VO}_{2.333}$, with water in small sealed gold tubes in an autoclave for 3 days at 550°C and 200 MPa (2 kbar) (cf. Andersson, 1967). The product contained well shaped black prismatic crystals together with small amounts of V_2O_5 . The cell dimensions of the product, derived from a powder photograph, were found to be the same as those given in Table 2, within the limits of error.

Table 2. *The crystal structure of V_3O_7*

Space group:	$C2/c$ (No. 15)		
Unit-cell dimensions:	$a=21.921$ (3) Å		
	$b=3.679$ (1)		
	$c=18.341$ (2)		
	$\beta=95.61$ (1)°		
Unit-cell content:	12 V_3O_7		
	Point set	Numbering of the atoms	
4(e)	0	\bar{y}	$\frac{3}{4}$ (n, 1)
	0	y	$\frac{1}{4}$ (n, 2)
	$\frac{1}{2}$	$\frac{1}{2}-y$	$\frac{3}{4}$ (n, 3)
	$\frac{1}{2}$	$\frac{1}{2}+y$	$\frac{1}{4}$ (n, 4)
8(f)	x	y	z (n, 1)
	\bar{x}	\bar{y}	\bar{z} (n, 2)
	\bar{x}	y	$\frac{1}{2}-z$ (n, 3)
	x	\bar{y}	$\frac{1}{2}+z$ (n, 4)
	$\frac{1}{2}+x$	$\frac{1}{2}+y$	z (n, 5)
	$\frac{1}{2}-x$	$\frac{1}{2}-y$	\bar{z} (n, 6)
	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$ (n, 7)
	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$ (n, 8)

Data collection

A well shaped prismatic crystal with the dimensions: $0.0464(a) \times 0.1436$ (along the unique b axis) $\times 0.0530$ (c) mm was selected and mounted along the prism axis. Preliminary investigations by means of oscillation and Weissenberg photographs proved it to be suitable for diffraction work. A Siemens automatic four-circle diffractometer equipped with a scintillation counter of NaI(Tl) type and a pulse-height discriminator was used for data collection with niobium-filtered $\text{Mo } K\alpha$ radiation. The $\theta-2\theta$ scan technique was employed, with the five-point measuring procedure. The scan range for the individual lattice points was given by the ex-

pressions: $-\Delta\theta=0.05+2 \text{ tg } \theta$, $+\Delta\theta=0.19+2 \text{ tg } \theta$. The count was taken in 0.01° steps, with the maximum step time of 1.2 s. For strong reflexions the step time was automatically reduced in order to accelerate the data collection. In order to keep counting losses low for strong reflexions the automatic attenuator mechanism was set to add attenuation filters. Three standard reflexions were measured every second day in order to keep a running check on the crystal orientation.

An estimated standard deviation for the net intensity was obtained from the expression $\sigma(I)=(I_b+I_t)^{1/2}$, where I_t and I_b are the total and background counts. 2131 independent lattice points up to $\theta=30.0^\circ$ were measured, of which 184 had a net count somewhat below the background count. Another 414 reflexions were judged insignificant for the refinement since they did not fulfil the criterion $\sigma(F_o)/|F_o| \leq 0.20$. The number of non-equivalent reflexions remaining was 1533. These $|F_o|$ values were used in the refinement.

Lorentz, polarization and absorption corrections were then applied to the data. The linear absorption coefficient $\mu(\text{Mo } K\alpha)=59.3 \text{ cm}^{-1}$ was used in calculating the absorption factor for each reflexion (*International Tables for X-ray Crystallography*, 1962). This was done by means of the Gaussian integration method, with $6 \times 10 \times 6$ gridpoints. The factor (A) in the formula $I=I_{\text{obs}}/A$ ranged from 0.716 to 0.779.

The calculations were performed on IBM 1800 and IBM 360/75 computers. The programs used are the same as those listed in the report on V_6O_{13} (Wilhelmi, Waltersson & Kihlberg, 1971).

Refinement

For the new Weissenberg photographs the observed systematic absences were the same as those reported by Andersson, Galy & Wilhelmi (1971), indicating that the space groups $C2/c$ (No. 15) and Cc (No. 9) (*International Tables for X-ray Crystallography*, 1952) were possible. The approximate structure indicated in the drawing given in the short communication was used as a starting point for the refinement. The parameters were: 44 positional parameters, 16 individual isotropic temperature-factor coefficients, one scale factor and one secondary extinction parameter. The scattering factors used were for neutral atoms (McMaster, Kerr Del Grande, Mallett & Hubbel, 1969), and the $\Delta f'$ and $\Delta f''$ values for $\text{Mo } K\alpha$ radiation were taken from *International Tables for X-ray Crystallography* (1962).

The quantity minimized in the least-squares refinement was

$$\sum w(|F_o| - |F_c|)^2.$$

The R value ($=\sum ||F_o| - |F_c||/|F_o|$) dropped rapidly to 0.0353. The weighted R_w value defined by the expression $R_w=(\sum w\Delta^2)^{1/2}/(\sum wF_o^2)^{1/2}$, was at this stage, 0.0371.

The isotropic temperature factors were in the range 0.35–0.67 for the vanadium atoms and varied between 0.46 and 1.06 for the oxygen atoms.

The refinement was now continued with anisotropic temperature factors. This increased the number of parameters as 92 anisotropic temperature factors had to be calculated, compared with 16 in the isotropic case. The *R* value (anisotropic refinement) finally obtained was 0.0279 and the weighted *R_w* value was 0.0294.*

The weights applied were calculated according to the formula

$$w = (\sigma^2(|F_o|) + a + b|F_o| + c|F_o|^2 + d|F_o|^3)^{-1}.$$

In the final cycle the constants were as follows:

$$a = 3.0, \quad b = -1.0 \times 10^{-2}, \quad c = -1.0 \times 10^{-4}, \\ \text{and} \quad d = 3.0 \times 10^{-6}.$$

* The final *F_o*, *F_c* tables have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30551 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Positional and thermal parameters

(a) Fractional coordinates

Atom (n)	Point set	x	y	z
V(1)	4(e)	0	0.81087 (26)	$\frac{1}{2}$
V(2)	8(f)	0.19549 (3)	0.82011 (15)	0.94140 (3)
V(3)	8(f)	0.03054 (2)	0.74814 (17)	0.94466 (3)
V(4)	8(f)	0.16289 (2)	0.74506 (17)	0.75467 (3)
V(5)	8(f)	0.32839 (3)	0.74538 (17)	0.87378 (3)
O(1)	4(e)	0	0.2507 (12)	$\frac{1}{2}$
O(2)	8(f)	0.19225 (11)	0.2588 (7)	0.93942 (13)
O(3)	8(f)	0.02324 (11)	0.2502 (7)	0.97363 (13)
O(4)	8(f)	0.32613 (12)	0.7456 (8)	0.76740 (13)
O(5)	8(f)	0.31591 (11)	0.2463 (7)	0.84644 (13)
O(6)	8(f)	0.20443 (11)	0.7473 (8)	0.83572 (13)
O(7)	8(f)	-0.00324 (11)	0.7516 (8)	0.85923 (13)
O(8)	8(f)	0.39756 (11)	0.7436 (8)	0.90628 (14)
O(9)	8(f)	0.08991 (11)	0.7491 (9)	0.76677 (14)
O(10)	8(f)	0.10538 (10)	0.7557 (8)	0.93727 (14)
O(11)	8(f)	0.28669 (10)	0.7522 (8)	0.95186 (12)

Table 3 (cont.)

(b) Final anisotropic temperature factors defined as $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The values given are $\beta_{ij} \times 10^5$. Estimated standard deviations are given in parentheses. The r.m.s. components (*R_i*) of thermal displacement along the ellipsoid axes and the r.m.s. radial (*R*) thermal displacement are included.

Atom (n)	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	<i>R</i> ₁	<i>R</i> ₂	<i>R</i> ₃	<i>R</i>
V(1)	25 (1)	1735 (67)	52 (2)	0	3 (1)	0	0.072	0.094	0.109	0.106
V(2)	19 (1)	376 (38)	33 (1)	3 (5)	3 (1)	3 (6)	0.051	0.062	0.078	0.113
V(3)	17 (1)	547 (35)	35 (1)	-4 (6)	8 (1)	-3 (7)	0.052	0.061	0.080	0.116
V(4)	24 (1)	548 (35)	25 (1)	-3 (6)	4 (1)	-2 (7)	0.061	0.064	0.076	0.117
V(5)	29 (1)	625 (36)	30 (1)	3 (5)	10 (1)	4 (6)	0.064	0.066	0.087	0.127
O(1)	74 (7)	984 (238)	67 (9)	0	6 (7)	0	0.082	0.106	0.134	0.190
O(2)	48 (5)	471 (156)	67 (6)	-29 (28)	4 (4)	19 (35)	0.055	0.106	0.110	0.162
O(3)	40 (5)	323 (158)	72 (6)	-23 (25)	22 (4)	-16 (30)	0.046	0.084	0.119	0.153
O(4)	82 (5)	492 (157)	37 (6)	38 (27)	15 (5)	13 (30)	0.057	0.076	0.141	0.170
O(5)	55 (5)	386 (152)	48 (6)	22 (25)	24 (4)	10 (28)	0.051	0.075	0.123	0.153
O(6)	47 (5)	1366 (171)	44 (6)	4 (29)	-5 (4)	51 (34)	0.078	0.100	0.112	0.169
O(7)	34 (4)	1530 (175)	57 (6)	-78 (30)	3 (4)	-5 (35)	0.077	0.098	0.113	0.168
O(8)	32 (4)	2639 (195)	86 (7)	15 (28)	2 (4)	-16 (36)	0.088	0.121	0.135	0.201
O(9)	26 (4)	2246 (189)	93 (7)	-3 (32)	9 (4)	-41 (40)	0.078	0.119	0.130	0.193
O(10)	19 (4)	1124 (166)	102 (7)	-7 (27)	11 (4)	22 (37)	0.066	0.082	0.132	0.171
O(11)	18 (4)	1276 (161)	31 (6)	-39 (28)	4 (4)	91 (34)	0.050	0.070	0.104	0.135

An isotropic model of the thermal movements of the atoms can be rejected at less than the 0.005 level (Hamilton, 1965).

The positional and thermal parameters, together with their standard deviations, are shown in Table 3.

The e.s.d. for the positional parameters are all of reasonable magnitudes (see Table 3). No attempt was therefore made to continue the refinement in the non-centrosymmetric space group *Cc* (No. 9).

Description and discussion of the crystal structure

The crystal structure of V₃O₇ is shown in Fig. 1. The unit cell contains 36 vanadium atoms; 12 are inside octahedra and 24 are five-coordinated. It is convenient when discussing the structure to consider it as being composed of four different kinds of chains and strings which extend parallel to the *b* axis, *viz.*

- I Single chains of V(1)O₆ octahedra linked by corners [Fig. 2(a)].
- II Double chains of pairs of edge-sharing V(2)O₆ octahedra linked by corners [Fig. 2(b)].
- III Zigzag strings of V(3)O₅ polyhedra joined by edges [Fig. 2(c)].
- IV Zigzag strings of V(4)O₅ and V(5)O₅ polyhedra joined by edges [Fig. 2(d)].

The chains and strings are joined parallel to the *ac* plane by additional common corners in a rather complicated way, to form a three-dimensional framework.

The structure elements I–IV will now be discussed in turn (*cf.* Table 4, which gives a survey of relevant V–O distances and O–V–O angles).

I. Each V(1)O₆ octahedron has two vertices in common with other octahedra in the same chain and shares four corners with the structure elements III and IV. The metal atom is displaced 0.22 Å from the equatorial plane formed by the atoms O(7,1), O(7,3), O(9,1) and O(9,3), forming a short V(1)–O(1,1) distance of 1.618 Å

The angle between the planes formed by the oxygens O(5,7)'-O(4,7)-O(11,7) and O(5,7)-O(4,7)-O(11,7) is 171° [see Fig. 2(d)]. The corresponding angles for the V(3)O₅ and V(4)O₅ polyhedra are 161 and 154°, respectively. It seems justified to describe the V(5)O₅ polyhedron as a square pyramid and the V(4)O₅ as a trigonal bipyramid, according to the external shape of the oxygen polyhedron.

Table 4. *Interatomic distances (Å) and bond angles (°) in V₃O₇*

Estimated standard deviations in the last decimal place are given in parentheses. The atoms are numbered as in Table 2.

(a) Structure element I, the single chain of octahedra

V(1,1)-O(1,1)'	1.618 (4)		
O(9,1)	1.978 (2)		
O(9,3)	1.978 (2)		
O(7,1)	2.023 (2)		
O(7,3)	2.023 (2)		
O(1,1)	2.061 (4)		
		Bond angles at V(1,1)	Distances between the oxygen atoms
O(1,1)-V(1,1)-O(1,1)'	179.9 (-)		3.679 (1)
O(1,1) O(7,1)	83.8 (1)		2.728 (4)
O(1,1) O(7,3)	83.8 (1)		2.728 (4)
O(1,1) O(9,1)	83.4 (1)		2.687 (4)
O(1,1) O(9,3)	83.4 (1)		2.687 (4)
O(1,1)' O(7,1)	96.2 (1)		2.723 (4)
O(1,1)' O(7,3)	96.2 (1)		2.723 (4)
O(1,1)' O(9,1)	96.6 (1)		2.695 (4)
O(1,1)' O(9,3)	96.6 (1)		2.695 (4)
O(7,1) O(7,3)	167.6 (2)		4.023 (5)
O(7,1) O(9,1)	88.0 (1)		2.779 (4)
O(7,1) O(9,3)	90.6 (1)		2.845 (4)
O(7,3) O(9,1)	90.6 (1)		2.845 (4)
O(7,3) O(9,3)	88.0 (1)		2.779 (4)
O(9,1) O(9,3)	166.8 (2)		3.930 (5)

(b) Structure element II, the double chain of octahedra

V(2,1)-O(2,1)'	1.615 (3)		
O(11,6)	1.977 (2)		
O(10,1)	1.983 (2)		
O(6,1)	1.985 (2)		
O(11,1)	2.005 (2)		
O(2,1)	2.066 (3)		
		Bond angles at V(2,1)	Distances between the oxygen atoms
O(2,1)-V(2,1)-O(2,1)'	175.2 (2)		3.679 (1)
O(2,1) O(6,1)	81.6 (1)		2.649 (4)
O(2,1) O(10,1)	81.2 (1)		2.637 (4)
O(2,1) O(11,1)	84.8 (1)		2.746 (4)
O(2,1) O(11,6)	83.5 (1)		2.692 (4)
O(2,1)' O(6,1)	97.0 (1)		2.707 (4)
O(2,1)' O(10,1)	94.4 (1)		2.653 (4)
O(2,1)' O(11,1)	99.7 (1)		2.778 (4)
O(2,1)' O(11,6)	99.2 (1)		2.746 (4)
O(6,1) O(10,1)	98.0 (1)		2.996 (3)
O(6,1) O(11,1)	83.3 (2)		2.653 (3)
O(6,1) O(11,6)	156.9 (1)		3.882 (3)
O(10,1) O(11,1)	165.6 (1)		3.957 (3)
O(10,1) O(11,6)	97.0 (1)		2.965 (3)
O(11,1) O(11,6)	77.9 (1)		2.502 (4)

Metal-metal separations (< 3.500 Å)

V(2,1)-V(2,6)	3.097 (1)
V(5,1)	3.288 (1)
V(4,1)	3.440 (1)
V(5,6)	3.489 (1)

Table 4 (cont.)

(c) Structure element III, the zigzag string of trigonal bipyramids

V(3,1)-O(10,1)	1.660 (2)
O(7,1)	1.666 (2)
O(3,1)	1.918 (3)
O(3,1)'	1.933 (3)
O(3,2)	1.995 (2)
V(3,1)···O(8,6)	3.019 (3)

	Bond angles at V(3,1)	Distances between the oxygen atoms
O(3,1)-V(3,1)-O(3,1)'	145.6 (1)	3.679 (1)
O(3,1) O(3,2)	73.9 (1)	2.354 (5)
O(3,1) O(7,1)	103.1 (1)	2.811 (4)
O(3,1) O(10,1)	98.6 (1)	2.717 (4)
O(3,1)' O(3,2)	73.7 (1)	2.357 (5)
O(3,1)' O(7,1)	102.1 (1)	2.805 (4)
O(3,1)' O(10,1)	96.6 (1)	2.689 (4)
O(3,2) O(7,1)	117.7 (1)	3.139 (3)
O(3,2) O(10,1)	136.3 (1)	3.395 (3)
O(7,1) O(10,1)	106.0 (1)	2.656 (3)
O(7,1)···V(3,1)···O(8,6)	174.8 (1)	4.681 (4)

Metal-metal separations (< 3.50 Å)

V(3,1)-V(3,2)	3.127 (1)
V(3,1)-V(3,2)'	3.143 (1)

(d) Structure element IV, the zigzag string of trigonal bipyramids and square pyramids

V(4,1)-O(9,1)	1.637 (3)	V(5,7)-O(8,7)	1.574 (3)
O(6,1)	1.666 (2)	O(11,7)	1.773 (2)
O(4,7)	1.902 (3)	O(5,7)	1.916 (3)
O(4,7)'	1.905 (3)	O(5,7)'	1.922 (3)
O(5,7)	1.956 (2)	O(4,7)	1.947 (2)
V(4,1)···O(4,1)	3.563 (3)	V(5,7)···O(6,7)	2.739 (3)

	Bond angles at V(4,1)	Distances between the oxygen atoms
O(4,7)-V(4,1)-O(4,7)'	150.1 (1)	3.679 (1)
O(4,7) O(5,7)	75.7 (1)	2.368 (4)
O(4,7) O(6,1)	97.2 (1)	2.680 (4)
O(4,7) O(9,1)	100.6 (1)	2.727 (4)
O(4,7)' O(5,7)	75.5 (1)	2.364 (4)
O(4,7)' O(6,1)	96.6 (1)	2.672 (4)
O(4,7)' O(9,1)	99.5 (1)	2.709 (4)
O(5,7) O(6,1)	133.4 (1)	3.327 (3)
O(5,7) O(9,1)	117.0 (1)	3.068 (4)
O(6,1) O(9,1)	109.6 (1)	2.698 (3)
O(4,1)···V(4,1)···O(9,1)	168.5 (1)	5.177 (4)

Bond angles at V(5,7)

O(4,7)-V(5,7)-O(5,7)	75.5 (1)	2.364 (4)
O(4,7) O(5,7)'	75.5 (1)	2.368 (4)
O(4,7) O(8,7)	108.0 (1)	2.857 (4)
O(4,7) O(11,7)	147.7 (1)	3.573 (3)
O(5,7) O(5,7)'	146.9 (1)	3.679 (1)
O(5,7) O(8,7)	101.7 (1)	2.715 (4)
O(5,7) O(11,7)	98.8 (1)	2.803 (4)
O(5,7)' O(8,7)	102.1 (1)	2.728 (4)
O(5,7)' O(11,7)	97.2 (1)	2.774 (4)
O(8,7) O(11,7)	104.4 (1)	2.647 (3)
O(8,7)···V(5,7)···O(6,7)	172.6 (1)	4.304 (4)

Metal-metal separations (< 3.500 Å)

V(4,1)-V(5,7)	3.009 (1)
V(4,1)-V(5,7)'	3.011 (1)
V(4,1)-V(2,1)	3.440 (1)

Metal-metal separations (< 3.500 Å)

V(5,7)-V(4,1)'	3.009 (1)
V(5,7)-V(4,1)	3.011 (1)
V(5,7)-V(2,7)	3.288 (1)
V(5,7)-V(2,4)	3.489 (1)

The different functions of the oxygen atoms can be summarized in the following way (see also Table 5). The four oxygen atoms O(3), O(4), O(5) and O(11) belong to three V–O polyhedra, and the mean values of the O–V distances are in the range 1.92–1.95 Å. For the O(2), O(6), O(7), O(9) and O(10) atoms, which are common to two V–O polyhedra, the corresponding distances are 1.81–1.84 Å. The 11th oxygen atom is bonded to one vanadium atom only [O(8)–V distance 1.574 Å].

If the cation and anion coordination numbers are considered, the formula of the compound can be written $[^{6+}V_3]^{13}[O_8]^{2-}[O_{11}]^{1-}[O_2]$.

The zigzag strings, built up by the edge-sharing oxygens O(3), O(4) and O(5), run infinitely in the **b** direction, while O(11) takes part in finite edge-sharings in the *ac* plane. This is reflected in the individual O–V distances, which are very close to the mean values for the former, while the corresponding distances for O(11) range from 1.773 to 2.005 Å. This difference in function is also shown in the V–O–V angles. The positions of the oxygens in relation to the planes formed by their metal coordination are visualized in the sums of the V–O–V angles for the different oxygen atoms. The oxygens with CN=2 have one short and one long oxygen–metal separation, but the averages differ very little for the different oxygens. The linearity of the vanadium coordination is reflected in the V–O–V angle.

Table 6 gives a survey of averaged vanadium–oxygen distances for a large number of binary and ternary vanadium oxide compounds. The vanadium atoms are in different oxidation states, exhibiting various coordination numbers.

The mean values of the V–O bond distances for the five different vanadium atoms in V_3O_7 are as follows: V(1) 1.947, V(2) 1.938, V(3) 1.834, V(4) 1.813 and V(5) 1.826 Å. These values are to be compared with the bond distances 1.94 and 1.81 Å, postulating 0.59, 0.46 and 1.35 Å for the V^{4+} (CN=6), V^{5+} (CN=5) and O^{2-} (CN=2, average) radii (*cf.* Table 6). The agreement between calculated and observed distances is satisfactory if it is assumed that the V^{4+} ions are situated in the octahedra and the V^{5+} ions in the bipyramids (see also Casalot, 1972).

In V_6O_{13} the averaged V–O distances are 1.923, 1.930 and 1.942 Å, respectively, which might indicate a more disordered distribution of the V^{4+} and the V^{5+} ions (*cf.* however Goodenough, 1972).

Magnetic and electrical properties of V_3O_7

The magnetic susceptibility measurements were carried out by the Faraday method over the range 78 to 270 K (Fig. 3) with a polycrystalline sample, prepared as previously described. The absolute susceptibility value of the standard substance used, $HgCo(SCN)_4$, was taken from Candela & Mundy (1962). Corrections for the diamagnetism of the ion cores were introduced into the calculations according to Selwood (1956).

If it is assumed that the orbital contribution to the magnetic moment is negligible the effective moment per V atom for V_3O_7 should be 1.00 B.M. if the formula is $V_2^{5+}V^{4+}O_7$. The mean value of several runs was 1.02 B.M. for the V_3O_7 sample, in good agreement with the calculated value for a distribution of formal oxidation states according to the observed structure

Table 5. *The environment of the oxygen atoms in V_3O_7*

Oxygen–metal	Distances (Å)	Mean values	Metal–oxygen–metal angles (°)	The sum of V–O–V angles (°)
O(3, 1)–V(3, 1)	1.918		V(3, 1)–O(3, 1)–V(3, 1)'	145.6
O(3, 1)–V(3, 1)'	1.933	1.949	V(3, 1)–O(3, 1)–V(3, 2)	106.1
O(3, 1)–V(3, 2)	1.995		V(3, 1)–O(3, 1)–V(3, 2)	106.3
O(4, 7)–V(4, 1)	1.902		V(4, 1)–O(4, 7)–V(4, 1)'	150.1
O(4, 7)–V(4, 1)'	1.905	1.918	V(4, 1)–O(4, 7)–V(5, 7)	102.9
O(4, 7)–V(5, 7)	1.947		V(4, 1)–O(4, 7)–V(5, 7)	102.8
O(5, 7)–V(5, 7)	1.916		V(5, 7)–O(5, 7)–V(5, 7)'	146.9
O(5, 7)–V(5, 7)'	1.922	1.931	V(5, 7)–O(5, 7)–V(4, 1)	102.1
O(5, 7)–V(4, 1)	1.956		V(5, 7)–O(5, 7)–V(4, 1)	101.8
O(11, 1)–V(5, 1)	1.773		V(5, 1)–O(11, 1)–V(2, 6)	136.9
O(11, 1)–V(2, 6)	1.977	1.918	V(5, 1)–O(11, 1)–V(2, 1)	120.8
O(11, 1)–V(2, 1)	2.005		V(2, 6)–O(11, 1)–V(2, 1)	102.1
O(1, 1)–V(1, 1)'	1.618	1.840	V(1, 1)–O(1, 1)–V(1, 1)	180.0
O(1, 1)–V(1, 1)	2.061			
O(2, 1)–V(2, 1)'	1.615	1.841	V(2, 1)–O(2, 1)–V(2, 1)	175.2
O(2, 1)–V(2, 1)	2.066			
O(6, 1)–V(4, 1)	1.666	1.826	V(4, 1)–O(6, 1)–V(2, 1)	140.8
O(6, 1)–V(2, 1)	1.985			
O(7, 1)–V(3, 1)	1.666	1.845	V(3, 1)–O(7, 1)–V(1, 1)	151.2
O(7, 1)–V(1, 1)	2.023			
O(9, 1)–V(4, 1)	1.637	1.808	V(4, 1)–O(9, 1)–V(1, 1)	162.3
O(9, 1)–V(1, 1)	1.978			
O(10, 1)–V(3, 1)	1.660	1.822	V(3, 1)–O(10, 1)–V(2, 1)	171.0
O(10, 1)–V(2, 1)	1.983			
O(8, 7)–V(5, 7)	1.574			

determination. The corresponding value of the Curie constant, computed from the expression $p_{\text{eff}} = 2.84\sqrt{C}$, is $1.62 \times 10^{-6} \text{ m}^3 \text{ K mol}^{-1}$ (0.129 unrationalized c.g.s. e.m.u. K mol^{-1}). This is in agreement with the C value 0.14 (c.g.s. units) reported by Kosuge (1967), but not with the magnetic data given by Tridot & Tudo (1966).

It should be noted that V_3O_7 , as well as V_6O_{13} , exhibits semiconductor behaviour (Toda, Kosuge & Kachi, 1966). For V_6O_{13} there exists a semiconductor-semiconductor transition at about 156 K (Kachi, Takada & Kosuge, 1963). However, the members of the homologous series of Magnéli phases, $\text{V}_n\text{O}_{2n-1}$, are better electrical conductors by several orders of magnitude than V_6O_{13} and V_3O_7 . Comparing V_6O_{13} and V_3O_7 with each other, V_3O_7 shows a lower conductivity than V_6O_{13} . This behaviour seems to be in good

agreement with the assumptions of the above-mentioned charge distribution in these two oxides.

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Table 6. Comparison of averaged V–O bond lengths, as a function of CN and oxidation number

The e.s.d. column lists the largest standard deviation of an individual bond length (Å) in each crystallographically independent polyhedron. The observed distances are compared with calculated values based on 'effective ionic radii' according to Shannon & Prewitt (1969). For convenience, different CN's for oxygens are considered. The compounds with mixed oxidation numbers for vanadiums are given separately.

Compound	E.s.d.	[⁶]V ³⁺	[⁵]V ⁴⁺	[⁶]V ⁴⁺	[⁴]V ⁵⁺	[⁵]V ⁵⁺	[⁶]V ⁵⁺	Reference	
V ₂ O ₃ (corundum)	0.001	2.010						Dernier (1970)	
V ₂ O ₃ (mon)	0.014	2.018						Dernier & Marezio (1970)	
VO(OH) (montroseite)	0.02	2.03						Evans & Mrose (1955)	
CaV ₃ O ₇	{ 0.03 0.03		1.89 1.89					} Bouloux & Galy (1973a)	
CaV ₄ O ₉	0.02		1.90						
VO ₂ (mon)	0.0012			1.9370				Bouloux & Galy (1973b)	
CuVO ₃	0.003			1.935				Longo & Kierkegaard (1970)	
VO ₂ (paramontroseite)	0.07			1.97				Rea, Bless & Kostiner (1972)	
β-VOSO ₄	0.018			2.002				Evans & Mrose (1955)	
VOSO ₄ ·3H ₂ O	0.003			2.001				Kierkegaard & Longo (1965)	
VOSO ₄ ·5H ₂ O	0.006			1.986				Théobald & Galy (1973)	
KVO ₃	0.01				1.73			Ballhausen, Djurinskij & Watson (1968)	
Cu ₅ V ₂ O ₁₀	{ 0.005 0.005				1.722 1.725			Evans (1960)	
YVO ₄	0.008				1.706			Shannon & Calvo (1973)	
Cu ₃ V ₂ O ₈	0.005				1.726			Baglio & Gashurov (1968)	
Ca ₂ VO ₄ Cl	0.001				1.707			Shannon & Calvo (1972)	
V ₂ O ₅	0.004					1.828		Banks, Greenblatt & Post (1970)	
KVO ₃ ·H ₂ O	0.02					1.83		Bachmann, Ahmed & Barnes (1961)	
β-VOPO ₄	0.007					1.818		Evans (1960)	
α-CdV ₂ O ₆	0.03					1.83		Gopal & Calvo (1972)	
CaV ₂ O ₆	0.03					1.81		Bouloux, Perez & Galy (1972)	
CuV ₂ O ₆	0.002					1.825		Bouloux, Perez & Galy (1972)	
CsV ₃ O ₈	0.020					1.816	1.920	Calvo & Manolescu (1973)	
KV ₃ O ₈	0.08					1.84	1.89	Evans & Block (1966)	
V ₁₀ O ₂₈ ⁶⁻ ion	{ 0.008 0.008 0.009 0.007 0.008						1.917 1.913 1.932 1.914 1.932	} Evans (1966)	
	{ 0.11 0.07						1.91 1.92		
	{ 0.03	1.88				1.83			Caughlan, Smith & Watenpugh (1966)
	{ 0.005 0.004		1.923 1.942				1.930		Galy, Darriet & Hagenmuller (1971)
	{ 0.004 0.003 0.003		1.947 1.938			1.834 1.813 1.826			Wilhelmi <i>et al.</i> (1971)
V ₃ O ₇								Present work	
CN for O ²⁻	Calculated bond distances based on 'effective ionic radii'							Shannon & Prewitt (1969)	
II		1.99	1.94	1.71	1.81	1.89			
III		2.00	1.95	1.72	1.83	1.90			
IV		2.02	1.97	1.75	1.84	1.92			

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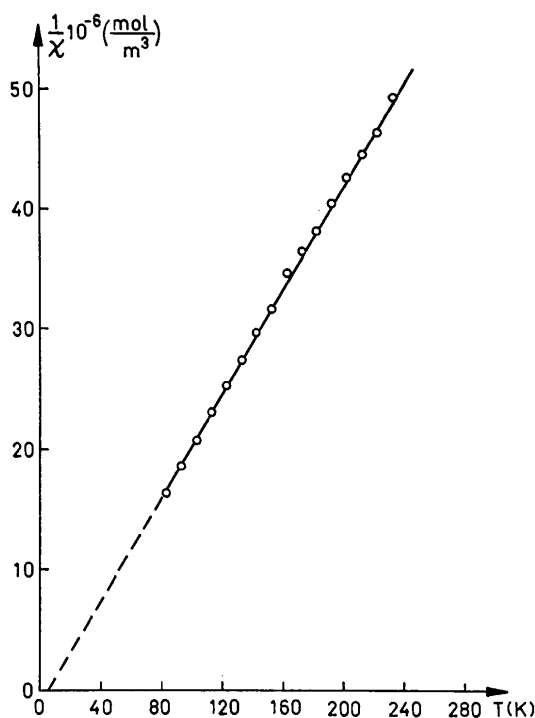


Fig. 3. The reciprocal magnetic susceptibility of V_3O_7 versus the temperature.

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