

## The Crystal Structure of and Valency Distribution in the Low-Temperature Modification of $V_3O_5$ . The Decisive Importance of a Few Very Weak Reflexions in a Crystal-Structure Determination

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(Received 21 July 1979; accepted 11 December 1979)

### Abstract

Low- $V_3O_5$ , monoclinic,  $P2/c$ . Unit-cell dimensions at 298 K:  $a = 9.859$  (1),  $b = 5.0416$  (5),  $c = 6.991$  (1) Å,  $\beta = 109.478$  (6)°.  $Z = 4$ ,  $D_m = 4.69$  (1),  $D_x = 4.720$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha, \lambda = 0.71069 \text{ \AA}) = 7.955$  mm<sup>-1</sup>. The crystal structure has been determined from X-ray single-crystal data collected with a PAILRED diffractometer at room temperature. The number of symmetry-independent reflexions with observable intensity was 2300, and the number of observations per variable was 29. The least-squares refinement ended with  $R = 0.025$ ,  $R_w = 0.028$ . There is complete separation between tri- and tetra-valent vanadium in low- $V_3O_5$ ; the higher-valent vanadium is situated at the shear planes. The space-group choice, based on the observation of only three very weak  $0k0$  reflexions, was quite decisive for this result.

### Introduction

In 1954, the existence of a vanadium oxide with composition  $VO_{1.67}$  was reported by Andersson (1954). From X-ray data and the observed density he judged the phase to have a centered monoclinic unit cell containing four  $V_3O_5$  formula units. On the basis of the photographic three-dimensional single-crystal X-ray data collected by Andersson, the crystal structure of  $V_3O_5$  was later studied (Åsbrink, Friberg, Magnéli & Andersson, 1959).

With the development of the technique of growing large single crystals of vanadium oxides using chemical transport with  $TeCl_4$  as a transport agent (Nagasawa, Bando & Takada, 1972), it also became possible to make X-ray diffraction experiments with larger crystals than before. Thus, Horiuchi, Tokonami, Morimoto, Nagasawa, Bando & Takada (1971) found that the diffraction record of  $V_3O_5$  contained many very weak peaks, a fact which contradicted the original supposition of a centered atomic arrangement. Single-crystal X-ray studies at room temperature of  $V_3O_5$

(Åsbrink, 1975) confirmed the existence of extra reflexions. However, whereas Horiuchi *et al.* did not observe any  $0k0$  reflexions with  $k$  odd, in the latter case a few very weak intensities of that kind were recorded, *single-diffraction conditions being satisfied*.

Another important discovery was made by Terukov & Chudnovskii (1974) in a study of the optical reflectivity and electrical conductivity of  $V_3O_5$  as functions of temperature. They found a semiconductor–semiconductor phase transition between 423 and 433 K. The existence of a phase transition was confirmed by the results of DTA measurements (Åsbrink, 1975), magnetic susceptibility measurements (Brückner, Wich, Terukov & Chudnovskii, 1975) and X-ray measurements on powder samples (Kartenko, Terukov & Chudnovskii, 1976; Brückner, Moldenhauer, Thuss & Försterling, 1976) and on single crystals (Hong & Åsbrink, 1977, 1980). In a recent article Chudnovskii, Terukov & Khomskii (1978) state that the transition is in fact of semiconductor–metal type even though the high-temperature phase is only ‘a poor metal’. A single-crystal investigation of the high-temperature modification of  $V_3O_5$  at 458 K (Hong & Åsbrink, 1977, 1980) revealed that all the extra reflexions from the low-temperature modification referred to above had disappeared and that the crystal structure, with a centered arrangement of the atoms, did not differ essentially from the one presented in 1959 as *the* crystal structure of  $V_3O_5$  (Åsbrink in the report of Magnéli, Andersson, Westman, Kihlberg, Holmberg, Åsbrink & Nordmark, 1959).

A crystal-structure determination of low- $V_3O_5$  was recently presented by Horiuchi, Morimoto & Tokonami (1976). Their result differs in important respects from the one obtained in this investigation.

### Experimental

The usual way of preparing a  $V_3O_5$  sample is to temper an appropriate mixture of  $V_2O_3$  and  $V_2O_5$  in an evacuated silica tube. However, even with tem-

peratures as high as 1373 K only very small crystals are produced. Crystals of a size satisfactory for X-ray single-crystal diffraction measurements cannot be obtained even after several weeks of heat treatment. As already mentioned, Nagasawa, Bando & Takada (1972) made large single crystals of  $V_3O_5$  by the chemical transport method with  $TeCl_4$  as a transport agent. In the present investigation crystals no larger than about  $0.01 \text{ mm}^2$  in cross-section were needed. Therefore, a simplified transport experiment was performed. The components were  $V_2O_5$  (Fisher Sc. Co., *p.a.*) and  $V_2O_3$  obtained from  $V_2O_5$  by reduction with hydrogen gas (Brauer, 1962). An appropriate mixture of the oxides together with a minute amount of  $TeCl_4$  was tempered in an evacuated silica tube in a vertical electric resistance furnace at 1373 K for about 5 d. A single crystal of rather irregular shape, with maximum lengths in three suitably chosen rectangular directions of  $\sim 0.14$ ,  $\sim 0.07$  and  $\sim 0.05 \text{ mm}$ , and of volume  $\sim 0.4 \times 10^{-3} \text{ mm}^3$  was picked out from the sample. Its *single-crystal* nature was ascertained from Weissenberg photographs.

The crystal was mounted on a PAILRED diffractometer in equi-inclination setting, with [001] parallel to the  $\omega$  axis. Monochromatic Mo  $K\alpha$  radiation was obtained by reflecting the primary beam at a take-off angle of  $6^\circ$  from the (002) plane of a graphite monochromator ( $\theta_M = 6.08^\circ$ ). The diameter of the primary-beam tunnel was 0.50 mm. A NaI-Tl scintillation detector was used together with a pulse-height analyzer. The intensities of all reflexions within two quadrants of each investigated reciprocal-lattice layer out to  $2\theta \simeq 100^\circ$  were measured. The number of layers was 13, corresponding to  $l$  values between 0 and 12, inclusive. The maximum attainable equi-inclination angle,  $\sim 41^\circ$ , permitted no  $l > 12$ . Reciprocal-lattice points too close to [001] to be attainable were investigated in a completing measurement with [010] parallel to the  $\omega$  axis. The 24 reflexions with the highest peak intensities were remeasured with lower X-ray tube power to avoid counting losses. Only three of them significantly improved (increased) their intensity after proper scaling. The intensity of each reflexion was measured with the  $\omega$ -scan method (moving crystal-stationary counter). With this method it is important to choose a sufficiently large aperture so that high-angle reflexions are not cut off by the detector aperture frame. An aperture of  $2^\circ$  was found sufficient in this case.

In low- $V_3O_5$  all reflexions with  $h + k + l$  odd are very weak. On the other hand, these odd reflexions contain the purest information about the deviation of the actual crystal structure from the formerly known idealized one. Thus, it was considered important to register them with as high a precision as reasonable. Therefore 'the automatic repeat of integrated-intensity scan' facility of PAILRED was used. This option

causes further scans, up to a maximum of  $n$ , to be made as long as the accumulated intensity is less than  $m$  counts;  $m$  and  $n$  being chosen among a limited number of alternatives. Here  $n = 5$  was always used, and  $m$  usually had the value 4000. By combining the repeated scan method with increased background measuring times, all weak reflexions, including the odd ones, were obtained with a comparatively good precision.

The unit-cell dimensions at 298 K were determined from a Guinier photograph of a powder specimen, with Cu  $K\alpha_1$  radiation and KCl as an internal standard. The density was determined by the loss of weight in benzene of a specimen consisting of a fine powder.

### Data reduction

The raw result from PAILRED was transformed to  $L_p$ -corrected net intensities with e.s.d.'s by the programs *PAIL* and *DATRED* (Brandt, 1971). The number of recorded independent reflexions was about 3600. 2300 of them were considered as observed since they satisfied the relation  $I_o > 2\sigma(I_o)$ . 713 of the latter had  $h + k + l = 2n + 1$  and were without exception very weak. Each of the about 1300 reflexions without significant intensity was finally given an intensity  $I_o = \frac{2}{3}\sigma(I_o)$ , *i.e.* one third of the threshold intensity (Hamilton, 1955). In the polarization correction the monochromator crystal was assumed to behave as an ideal mosaic crystal. As a general assumption this may certainly be doubted (Miyake, Togawa & Hosoya, 1964; Jennings, 1968; Olekhovich, 1969; Hope, 1971). However, in this case with the very low Bragg angle of the monochromator reflexion,  $\theta_M = 6.08^\circ$ , the error in the polarization factors applied should be negligible.

The intensities were corrected for absorption by the program *DATAP2* (Coppens, Leiserowitz & Rabinovich, 1965; local version). The linear absorption coefficient,  $\mu = 7.955 \text{ mm}^{-1}$ , was calculated from mass absorption coefficients given in *International Tables for X-ray Crystallography* (1974) and from the observed density,  $D_m = 4.69 \text{ Mg m}^{-3}$ . The rather irregular crystal was described by 16 plane surfaces, and the number of numerical integration elements was 480 ( $6 \times 8 \times 10$ ). The transmission factors varied from 0.53 to 0.75 for the reflexions  $\bar{3}10$  and 110, respectively. In connexion with the absorption calculations, preparatory calculations were also made in *DATAP2* for the secondary-extinction correction method according to Zachariasen (1967) which was modified for equi-inclination geometry by Åsbrink (1973).

### Structure determination

The only reflexions which are systematically absent in low- $V_3O_5$  are  $h0l$  with  $l = 2n + 1$ . The possible space

groups, then, are  $P2/c$  (No. 13) and  $Pc$  (No. 7). As mentioned above, an idealized crystal structure had been determined with space group  $I2/c$  (No. 15) ( $C2/c$  with the originally used unit cell). The atomic coordinates then obtained (Åsbrink in the report of Magnéli *et al.*, 1959) were used as the initial positional parameters in the present calculations which started with the assumption that  $Pc$  was the correct space group. It was thought advantageous to start with the assumption of the lower symmetry as false initial symmetries should then be more effectively avoided. In order to have the unit-cell origin on a  $c$ -glide plane, in accordance with *International Tables for X-ray Crystallography* (1952), the initial origin was moved to the point  $(\frac{1}{4}, -\frac{1}{4}, \frac{1}{4})$ . The original eightfold or fourfold atomic positions were all split up into twofold positions. In the least-squares calculations, using program *FALFA* (Koenig, 1971), atomic scattering factors including corrections for anomalous dispersion, for  $O^-$  and  $V^{(5/3)+}$  were used – the former directly obtained from *International Tables for X-ray Crystallography* (1974), the latter derived by interpolation between the  $f(V)$  and  $f(V^{2+})$  values given in the same source. The strategy of the least-squares calculations included initial fixation of every second atomic position. Furthermore, to begin with only partial data sets were used, limited upwards in  $\theta$  and exclusive of very strong reflexions. After alternating release of fixed positions, each including an isotropic thermal variable, and after successive inclusion of more data, an  $R$  value of 0.050 was obtained for all observed reflexions except the 342 strongest ones.

In the next step all positional variables were fixed and only one secondary-extinction variable (Zachariassen, 1967) was refined together with two scale factors and 16 isotropic thermal-vibration variables, one for each atomic position; this resulted in  $R = 0.034$  for all the 2434 observed reflexions.

Now, all atomic positions were released and refined anisotropically together with the extinction variable and the two scale factors, except that the  $x$  and  $z$  coordinates of one vanadium position were kept constant to fix the origin of the unit cell. With these 145 variables all the observed reflexions were used, and the final  $R$  was 0.024. The refinement of the extinction variable was now considered completed as the last shift was only about 3% of the e.s.d. Then a few final calculations remained for which averages were obtained for a few hundred symmetry-dependent reflexions after application of the extinction corrections. Then, the 2300 symmetry-independent extinction-corrected reflexions which remained could be used in the last least-squares cycles, which ended with  $R = 0.023$  and  $R_w = 0.026$ . Yet, the result was not satisfactory as  $\beta_{11}$  for one oxygen atom was negative. Furthermore, no less than 42 correlation coefficients had their absolute values equal to or larger than 0.80. *ORTEP* plots

[Johnson (1965); local version by I. Carlborn & A. G. Nord] of the six independent vanadium coordination octahedra also showed peculiarities in the direction and shape of many oxygen thermal-vibration ellipsoids. Finally, the estimated standard deviations for the atomic variables were larger than expected and showed remarkable variations.

Therefore, new least-squares calculations were started in which the space group was chosen as the centrosymmetric  $P2/c$ . These calculations, straightforward as they were, caused no trouble and ended in  $R = 0.025$  and  $R_w = 0.028$  for all the 2300 observed independent reflexions, the maximum parameter shift in the last refinement cycle being less than  $0.01\sigma$ . The weighting function used was  $w = [\sigma(F_o)]^{-2}$  where  $\sigma(F_o) = \sigma_{\text{stat}}(F_o) + 0.00002F_o^2(1 + 0.01|F_o|)$ . Its suitability was tested by weight analyses (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961). A structure factor calculation also including the 1299 symmetry-independent reflexions with  $\sigma(I_o)/I_o \geq 0.50$  gave  $R = 0.048$ , and the  $|F_c|$  values for the unobserved reflexions were all reasonably small. Now all thermal-vibration parameters had quite normal values and *ORTEP* plots of the four independent coordination octahedra also showed very reasonable thermal-vibration ellipsoids for all atoms (*cf.* Figs. 1–4). Furthermore, only 19 correlation coefficients had their absolute values larger than 0.50, the two largest being 0.72. Finally, the e.s.d.'s for the atomic variables were all smaller than those obtained in the  $Pc$  refinement, the average reduction factor being no less than three, and they were all fairly constant within groups of comparable quantities. Therefore, I conclude that the correct space group is  $P2/c$ .

The final atomic coordinates are presented in Table 1. The final value of the secondary-extinction parameter

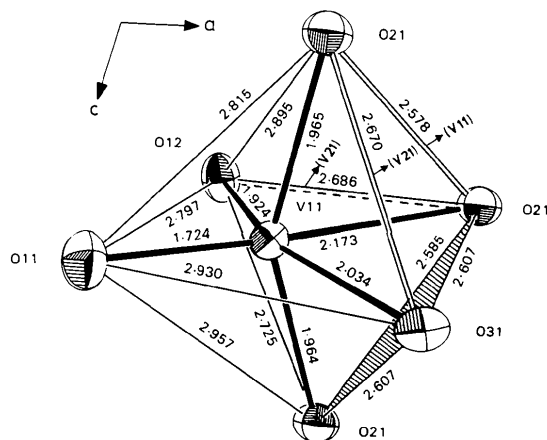


Fig. 1. Tetravalent vanadium atom, V(11), with oxygen coordination octahedron. The face in common with an octahedron around another V(11) atom is shaded. Edges shared with other octahedra are indicated by double lines.

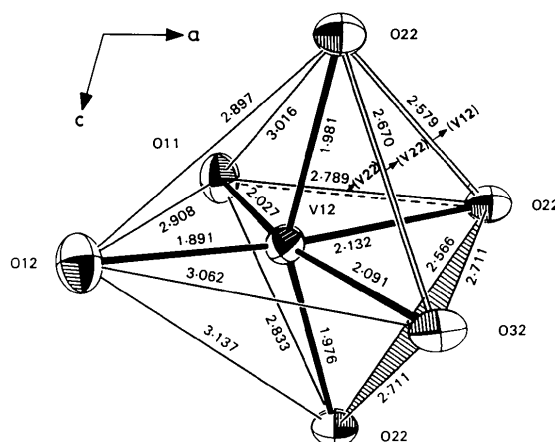


Fig. 2. Trivalent vanadium atom, V(12), with oxygen coordination octahedron. The face in common with an octahedron around another V(12) atom is shaded. Edges shared with other octahedra are indicated by double lines.

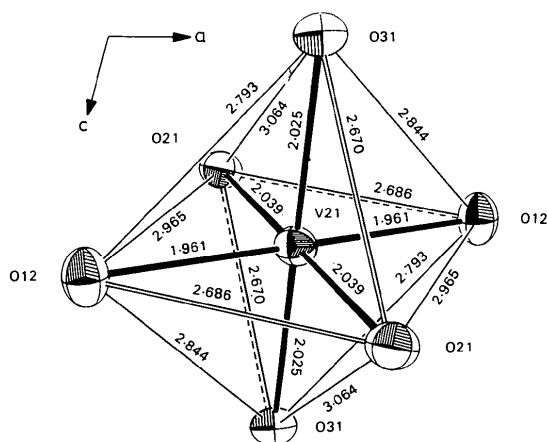


Fig. 3. Trivalent vanadium atom, V(21), with oxygen coordination octahedron. Edges shared with other octahedra, all containing V(11) atoms, are indicated by double lines.

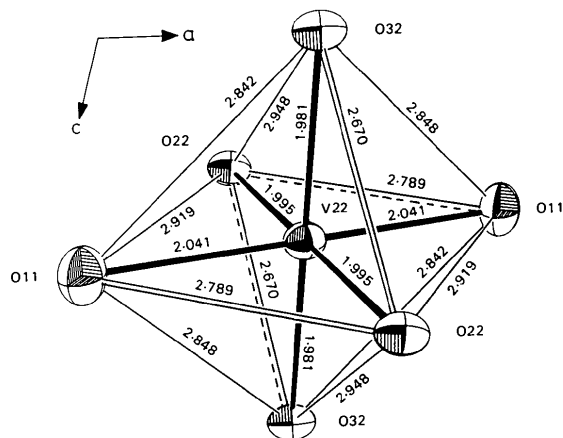


Fig. 4. Trivalent vanadium atom, V(22), with oxygen coordination octahedron. Edges shared with other octahedra, all containing V(12) atoms, are indicated by double lines.

$r\lambda^{-1}$  (Zachariasen, 1967) was  $3.98(10) \times 10^4$ . The reflexion most affected by extinction was  $\bar{3}10$  with the extinction factor  $y = 0.344$ . Interatomic distances calculated with program *DISTAN* (A. Zalkin, Berkeley, California, USA; local version by A. G. Nord & B. G. Brandt) are found in Table 2.\*

## Discussion

The crystal structure of low- $V_3O_5$  as well as of high- $V_3O_5$  can be described as a hexagonal close packing of oxygen atoms with the octahedral interstices partially filled with vanadium atoms. The vanadium-containing octahedra form chains of two types which run parallel to  $[001]$  and which alternate in the directions  $[100]$  and  $[010]$  (cf. Fig. 5). One type of chain is composed of double octahedra each of which is formed from two single octahedra sharing a face. The double octahedra are coupled together in the chain by having edges in common. The other type of chain is composed of single octahedra coupled together by sharing corners. The chains are mutually connected by sharing octahedral edges or corners.

Horiuchi *et al.* (1971) have pointed out that  $V_3O_5$  may be considered as one member of the homologous series  $V_nO_{2n-1}$  derived from the rufite structure by crystallographic shear ( $\bar{1}\bar{2}1$ ). On this basis the fourfold vanadium positions V(11) and V(12) in the double-octahedral chains of low- $V_3O_5$  are situated *at* the shear planes while the twofold positions V(21) and V(22) in the single octahedral chains are situated *between* the shear planes (cf. Fig. 6).

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35028 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters of low- $V_3O_5$  and isotropic temperature factors equivalent to the obtained anisotropic components

The first index of each position refers to the originally determined idealized structure of  $V_3O_5$  (Åsbrink in the report of Magnéli *et al.*, 1959). Thus, V(11) and V(12) originate from the eightfold position, V(1), of the idealized  $V_3O_5$  structure *etc.*

Fractional atomic coordinates  $x, y, z$  ( $\times 10^5$ ). Numbers in parentheses are e.s.d.'s in the least significant digits.

	P2/c	x	y	z	$B_{iso}$ (Å <sup>2</sup> )
V(11)	4(g)	13216 (2)	626 (4)	41073 (3)	0.329 (3)
V(12)	4(g)	37089 (2)	49659 (4)	9136 (3)	0.347 (3)
V(21)	2(c)	0	50000	0	0.338 (4)
V(22)	2(d)	50000	0	0	0.324 (4)
O(11)	4(g)	29983 (8)	14739 (19)	46191 (13)	0.522 (13)
O(12)	4(g)	18668 (8)	34014 (18)	2629 (13)	0.463 (12)
O(21)	4(g)	8201 (8)	15179 (19)	63923 (13)	0.423 (13)
O(22)	4(g)	42105 (8)	34123 (18)	86342 (12)	0.378 (13)
O(31)	2(e)	0	29721 (25)	25000	0.405 (17)
O(32)	2(f)	50000	18517 (26)	25000	0.388 (17)

Table 2. *Interatomic distances (Å) in the structure of low- $V_3O_5$* 

*e* or *f* next to an O—O distance means that the distance is a shared edge or part of a shared face respectively. *e* or *f* next to a V—V distance means that the distance is across a shared edge or across a shared face respectively. Averages in parentheses are corrected for the irregularity of the actual octahedron. Further numbers in parentheses are e.s.d.'s in the least significant digits.

V(11) octahedron		V(12) octahedron	
V(11)—O(11)	1.7240 (8)	V(12)—O(12)	1.8912 (8)
—O(12)	1.9240 (9)	—O(22)	1.9756 (9)
—O(21)	1.9638 (9)	—O(22)	1.9806 (9)
—O(21)	1.9650 (9)	—O(11)	2.0270 (10)
—O(31)	2.0336 (9)	—O(32)	2.0913 (10)
—O(21)	2.1734 (8)	—O(22)	2.1316 (8)
Average	1.9640 (1.9337)	Average	2.0162 (2.0060)
O(21)—O(21) <i>e</i>	2.578 (2)	O(22)—O(22) <i>e</i>	2.579 (2)
O(21)—O(21) <i>f</i>	2.585 (2)	O(22)—O(22) <i>f</i>	2.566 (2)
O(21)—O(31) <i>f</i> × 2	2.607 (2)	O(22)—O(32) <i>f</i> × 2	2.711 (2)
O(21)—O(31) <i>e</i>	2.670 (1)	O(22)—O(32) <i>e</i>	2.670 (1)
O(21)—O(12) <i>e</i>	2.686 (1)	O(22)—O(11) <i>e</i>	2.789 (1)
O(21)—O(12)	2.725 (2)	O(22)—O(11)	2.833 (1)
O(11)—O(12)	2.797 (2)	O(12)—O(11)	2.908 (2)
O(21)—O(11)	2.815 (1)	O(22)—O(12)	2.897 (1)
O(21)—O(12)	2.895 (2)	O(22)—O(11)	3.016 (2)
O(11)—O(31)	2.930 (1)	O(12)—O(32)	3.062 (1)
O(21)—O(11)	2.957 (1)	O(22)—O(12)	3.137 (1)
Average	2.738	Average	2.823
V(21) octahedron		V(22) octahedron	
V(21)—O(12) × 2	1.9609 (8)	V(22)—O(32) × 2	1.9815 (7)
—O(31) × 2	2.0249 (7)	—O(22) × 2	1.9954 (9)
—O(21) × 2	2.0392 (9)	—O(11) × 2	2.0414 (8)
Average	2.0083 (2.0064)	Average	2.0061 (2.0051)
O(21)—O(31) <i>e</i> × 2	2.670 (1)	O(22)—O(32) <i>e</i> × 2	2.670 (1)
O(21)—O(12) <i>e</i> × 2	2.686 (1)	O(22)—O(11) <i>e</i> × 2	2.789 (1)
O(12)—O(31) × 2	2.793 (1)	O(11)—O(32) × 2	2.842 (1)
O(12)—O(31) × 2	2.844 (1)	O(11)—O(22) × 2	2.848 (1)
O(12)—O(21) × 2	2.965 (2)	O(11)—O(22) × 2	2.919 (2)
O(21)—O(31) × 2	3.064 (2)	O(22)—O(32) × 2	2.948 (2)
Average	2.837	Average	2.836
V—V distances			
V(11)—V(11) <i>f</i>	2.8171 (4)	V(12)—V(12) <i>f</i>	2.7632 (4)
V(11)—V(21) <i>e</i>	2.9708 (3)	V(12)—V(22) <i>e</i>	2.9730 (3)
V(11)—V(21) <i>e</i>	3.0239 (3)	V(12)—V(22) <i>e</i>	3.0020 (3)
V(11)—V(11) <i>e</i>	3.2438 (4)	V(12)—V(12) <i>e</i>	3.2067 (4)

Of the four independent V—O octahedra, one, V(11)—O, is clearly set off from the rest by the average V—O bond length as well as by the average O—O distance (*cf.* Table 2 and Figs. 1–4). The V(11)—O octahedron is not only more contracted than the other three, it is also by far the most distorted one, as judged by the individual V—O distances. If one assumes that the logarithmic relation between bond strength and

bond length (Pauling, 1947; Zachariasen, 1978) is approximately correct, one can derive that the average bond length  $\overline{V-O}$  for an octahedron with a V atom of a given valency *increases* as the distortion of the octahedron increases. A correction term to be added to the observed  $\overline{V-O}$  value can be derived from that relation (*cf.* Allmann, 1975). Then, the 'corrected' average bond lengths correspond to ideal non-distorted octahedra and are the quantities which should be used in comparisons between octahedra regarding the valencies of their central atoms. In the present case such corrections were calculated from the relation given by Zachariasen (1978), which reads  $d_i = d(1(1$

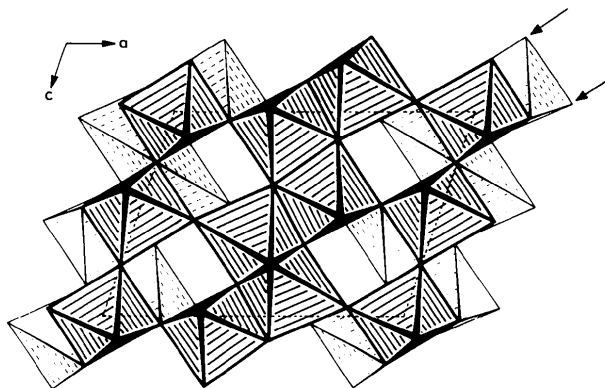


Fig. 5. The coupling of octahedra in  $V_3O_5$ , [010] projection of two layers of octahedra ( $y \approx 0$  and  $y \approx 0.5$  respectively). The two arrows limit a section which is presented in Fig. 6.

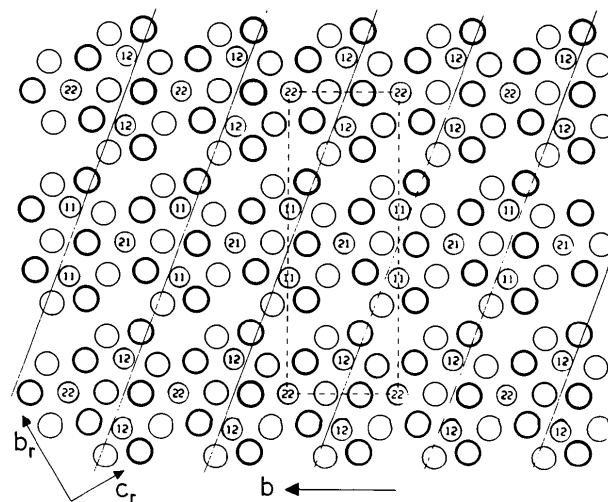


Fig. 6. A projection on (101) of the section between the arrows in Fig. 5 showing the hexagonal close packing of oxygen atoms in  $V_3O_5$  and the relation between the rutile and  $V_3O_5$  structures. The axes of the rutile subcell are denoted  $b$ , and  $c_r$ , respectively. Empty circles indicate oxygen atoms, circles marked with 11, 12, 21 and 22 indicate vanadium positions V(11), V(12), V(21) and V(22) respectively in the low- $V_3O_5$  structure. The full lines indicate the intersections of the slanting shear planes with (101) at  $x + z = 1$ .

– 0.171 ln  $S_i$ ); where  $d_i$  = observed bond length (Å),  $S_i$  = corresponding bond strength and  $d(1)$  is a constant which in the present case was chosen to be 1.799 Å. Then the correction term is

$$-d(1) 0.171 \ln \{ \bar{S} / (S_1 S_2 \dots S_6)^{1/6} \},$$

with

$$\bar{S} = \sum_{i=1}^6 S_i / 6.$$

The result of the application of these corrections to the observed  $\bar{V}-\bar{O}$  values was, firstly, that V(11) was further differentiated from the other three vanadium positions and, secondly, that the latter, closely resembling each other when still uncorrected, became even more similar (*cf.* Table 2). The calculation therefore gives strong support to the assumption that one of the vanadium positions, V(11), contains  $V^{IV}$  while the other three, V(12), V(21) and V(22), all contain  $V^{III}$ . Predicted  $V^{IV}-O$  and  $V^{III}-O$  distances, calculated from Shannon & Prewitt's (1969) (SP) radii, and taking account of the varying coordination numbers of the oxygen atoms, are longer, as expected, than the corrected experimental distances, since the SP radii are derived from sets of raw interatomic distances. For example, the  $V^{IV}$  radius published by SP is mainly based on data from  $VO_2$  (Longo & Kierkegaard, 1970) where the  $V^{IV}-O$  octahedron is rather irregular. A calculation, as above, of an irregularity correction to the average  $V-O$  bond length in  $VO_2$  yields  $\Delta = -0.019$  Å. One could thus define a  $V^{IV}$  radius for a regular octahedral environment which is smaller than the SP radius. It seems as if such 'normalized' radii would be even more useful to the crystallographer than the SP radii – indispensable as they are.

Bond-strength calculations using Zachariasen's equation with  $d(1) = 1.799$  gave the valencies (=bond-strength sums) 3.87, 3.06, 3.06 and 3.07 for V(11), V(12), V(21) and V(22) respectively. Considering the approximate character of the relation, I think that the deviations from the ideal values 4 and 3 respectively are sufficiently small not to disturb the conclusion reached above of a complete separation into  $V^{IV}$  and  $V^{III}$ .

With  $d(1) = 1.799$  the vanadium valency sum for the whole unit cell was 39.99, which should be compared with the ideal value of 40.00. With  $d(1) = 1.790$ , as recommended by Zachariasen (1978), the vanadium valencies add up to only 38.73. It might be that Zachariasen obtained the lower  $d(1)$  value in calculations on compounds of which several had strong  $V-V$  interactions, *e.g.*  $VO_2$  (insulator) and  $V_2O_3$  (metal). According to test calculations on various modifications of  $VO_2$  as well as on  $V_2O_3$  (metal) and  $V_2O_3$  (insulator), an increased metal-metal interaction generally leads to larger values for the bond-strength sums. Therefore, if one derives  $d(1)$  from structures

with considerable interactions of that kind, one will obtain slightly lower values than when using structures where such interactions are weaker or absent. The shortest  $V-V$  distance in low- $V_3O_5$  occurs across an octahedral face and is equal to 2.763 Å [V(12)–V(12)]. It should be compared with the corresponding value for  $V_2O_3$  (metal) which is 2.697 Å (Dernier, 1970). The shortest  $V-V$  distance across a common octahedral edge in low- $V_3O_5$  is 2.971 Å [V(11)–V(21)], in  $VO_2$  (insulator) the corresponding distance is 2.619 Å (Longo & Kierkegaard, 1970) and in  $V_2O_3$  (metal) the corresponding distance is 2.882 Å (Dernier, 1970). The metal-metal interactions in low- $V_3O_5$  are thus considerably weaker than corresponding interactions in  $V_2O_3$  (metal) and  $VO_2$  (insulator).

The tendency of the high-valent (smaller) atom to reside at the shear planes has been observed in several other oxides of the  $V_3O_5$  type. First of all, in high- $V_3O_5$  (Hong & Åsbrink, 1977, 1980) all, or in any case a very large part, of the  $V^{IV}$  atoms are situated in the chains of double octahedra. Furthermore, in the crystal structure of  $V_2TiO_5$  at room temperature, which was determined from neutron powder diffraction data (Åsbrink & Sävborg, 1980), all metal atoms *between* the shear planes were found to be  $V^{III}$ . Thus, the tetravalent metal atoms, which probably are  $Ti^{IV}$ , must be situated *at* the shear planes. Finally, for  $Ti_2CrO_5$ , investigated at room temperature in another neutron powder diffraction work (Åsbrink & Andresen, 1980), an analogous result was obtained (*cf.* Table 3).

A concentration of high-valent metal atoms at the shear planes has been observed in several molybdenum oxides with shear structures (Kihlberg, 1963). In at least one more vanadium oxide with a shear structure, *viz.*  $V_4O_7$  (metal), the same tendency was recently observed (Hodeau & Marezio, 1978). This general trend does not seem surprising since a smaller (high-valent) 'rattling' (Dunitz & Orgel, 1960) atom should fit better in a distorted environment than a larger (lower-valent) one, and the coordination around a metal atom naturally is less symmetric *at* a

Table 3. *The metal-atom valency distribution in a number of trimetal pentoxide phases with  $V_3O_5$  structure*

Structure type 'L' and 'H' indicates low- $V_3O_5$  and high- $V_3O_5$  structure, respectively. [ ], and [ ] means metal-atom position *at* a shear plane and *between* shear planes, respectively.

Phase	Structure type	Metal-atom valency distribution	Reference
Low- $V_3O_5$	L	$[V^{IV}]_1[V^{III}]_2[V^{III}]_1[V^{III}]_2O_5$	This work
High- $V_3O_5$	H	$[V^{IV}V^{III}]_1[V^{III}]_2O_5$	Hong & Åsbrink (1977, 1980)
$V_2TiO_5$	H*	$[V^{III}Ti^{IV}]_1[V^{III}]_2O_5$	Åsbrink & Sävborg (1980)
$Ti_2CrO_5$	H*	$[Ti^{IV}Ti^{III}_{0.69}Cr^{III}_{0.31}]_1[Ti^{III}_{0.31}Cr^{III}_{0.69}]_2O_5$	Åsbrink & Andresen (1980)

\* As single-crystal data are not yet available, H is assumed for simplicity. This choice has no effect on the conclusion drawn in the Discussion.

shear plane than *between* shear planes in a shear structure (*cf.* for example Fig. 6).

Regarding the bonding in the non-centrosymmetric [V(11) and V(12)] octahedra, Figs. 1 and 2 show that the shortest V—O bond engages the only oxygen atom in the respective coordination which belongs neither to a shared face nor to a shared edge. The longest V(11)—O and V(12)—O bond respectively, on the other hand, connects vanadium to the oxygen atom which is engaged in the largest number of edge and face sharings (*cf.* Figs. 1 and 2). These observations might mainly be explained as effects of repulsions between vanadium atoms. Then, the effect could be expected to be largest when the V—V repulsion across a common face or a common edge includes one or two V(11) (V<sup>IV</sup>) atoms; this is in accordance with the observations (*cf.* Table 2 and Figs. 1 and 2).

### Importance of the correct choice of space group

In the *Introduction*, it was mentioned that there is a discrepancy regarding the space group between the present result and that of certain Japanese colleagues. They chose the space group  $P2_1/c$  ( $P2_1/n$  with the original unit cell) since they did not observe any  $0k0$  reflexions with  $k$  odd, whereas I found the correct choice to be  $P2/c$ . We both started with the knowledge of the idealized V<sub>3</sub>O<sub>5</sub> structure which had been allotted the space group  $I2/c$  (No. 15) ( $C2/c$  with the original unit cell) (Åsbrink in the report of Magnéli *et al.*, 1959). The problem, then, was correctly to split each of the 8(4)-fold positions of the latter into two 4(2)-fold positions of one or the other of the former space groups. (Splitting of the 4-fold positions of the centered space group is required only with  $P2/c$ .) This problem is almost solved by a proper choice of origin in the centered space group. In the first alternative above one should take as the origin a point with symmetry  $\bar{1}$  on an  $a$ -glide plane of  $I2/c$  [corresponds to  $\bar{1}$  on  $c$  of  $C2/c$ , *i.e.* the original origin (*cf. loc. cit.*)]. With this choice of origin, the coordinates of the 8( $f$ ) equivalent sites are

$$(0,0,0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (x, y, z; x, \frac{1}{2} - y, \frac{1}{2} + z).$$

Removing the  $I$  centering gives 4( $e$ ) of  $P2_1/c$  (No. 14). In the second alternative one should place the origin at  $\bar{1}$  on a  $c$ -glide plane of  $I2/c$  (corresponds to  $\bar{1}$  on  $n$  of  $C2/c$ ). Then, the coordinates of the 8( $f$ ) equivalent sites are

$$(0,0,0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (x, y, z; x, \bar{y}, \frac{1}{2} + z).$$

Removing the  $I$  centering now yields 4( $g$ ) of  $P2/c$  (No. 13).

The different consequences of the two alternatives of splitting may be illustrated by an example. Below are presented the coordinates  $x, y, z$  of the 8( $f$ ) equivalent vanadium sites, V(1), in the idealized structure of V<sub>3</sub>O<sub>5</sub>,

with the origin of the unit cell on an  $a$  glide of  $I2/c$  (first alternative above), and also the coordinates  $x', y', z'$  of the same sites with the origin placed on a  $c$  glide (second alternative):

1000x	1000y	1000z		1000x'	1000y'	1000z'
A 619	245	340	Moving origin to ( $\frac{1}{4}, -\frac{1}{4}, \frac{1}{4}$ ) →	C 369	495	90
A 381	755	660		D 131	5	410
A 381	745	160		D 131	995	910
A 619	255	840		C 369	505	590
B 119	745	840		D 869	995	590
B 881	255	160		C 631	505	910
B 881	245	660		C 631	495	410
B 119	755	340		D 869	5	90

*N.b.* Sites  $A$  and  $B$  are pairwise related by  $I$  centering as are sites  $C$  and  $D$ .

The  $A$  and  $B$  sites, respectively, transform to two different sets of equivalent sites, 4( $e$ ), of  $P2_1/c$  whereas the  $C$  and  $D$  sites, respectively, transform to two different sets of equivalent sites, 4( $g$ ), of  $P2/c$ . As  $P2/c$  is the correct space group,  $C$  and  $D$  correspond to the (unrefined) vanadium positions V(12) and V(11) respectively (*cf.* Table 1), whereas 'position  $A$ ' is a mixture composed of two V(11) and two V(12) sites; and 'position  $B$ ' is, likewise, a mixture of the remaining two V(11) and two V(12) sites. As stated in the *Discussion*, V(11) was found to contain V<sup>IV</sup> and V(12) V<sup>III</sup>. Then, by refinement in space group  $P2_1/c$ , one obviously cannot detect this separation of the two valency states. The relative success of the refinement of the crystal structure of low-V<sub>3</sub>O<sub>5</sub> in the wrong space group  $P2_1/c$  is due to the existence of screw axes in the idealized structure.

In Table 4 a comparison is made between observed and calculated structure factor values for  $0k0$  reflexions with  $k = 2n + 1$ .

I wish to express my sincere gratitude to Professor A. Magnéli for his valuable criticism on the manuscript, to Dr S.-H. Hong for his competent assistance with the crystal measurements for the absorption correction, and to Dr S. Westman for his correction of the English of the paper.

Table 4.  $0k0$  reflexions,  $k = 2n + 1$ ; observed and calculated structure factors

$h k l$	$ F_o $	$F_c$
0 11 0	3.8	-3.3
0 9 0	<2.8	0.4
0 7 0	<2.7	2.5*
0 5 0	6.0	-6.1
0 3 0	<2.2	0.0
0 1 0	4.0	4.7

\* This non-observed reflexion was in fact observed at room temperature with the larger crystal used in the high-V<sub>3</sub>O<sub>5</sub> work.

This investigation is a part of a research program supported by the Swedish Natural Science Research Council.

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## The Structure Determination of a New Intermetallic Compound $K_3Ga_{13}$

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(Received 31 October 1979; accepted 6 February 1980)

### Abstract

The compound is orthorhombic; the unit cell with  $a = 6.441$  (3),  $b = 16.143$  (3),  $c = 28.404$  (7) Å contains eight formula units. Diffraction data with  $0 < 2\theta < 50^\circ$

(Mo  $K\alpha$  radiation) were collected on a Nonius CAD-4 automatic diffractometer within the octant  $hkl$ . The structure was solved in space group  $Cmcm$  by direct methods and refined by full-matrix least squares to a final  $R(F)$  of 5.6% for 1040 reflections with  $I > 3\sigma(I)$ .