

Fig. 3. Représentation schématique de  $\text{Cu}_2\text{Ag}_2\text{O}_{14}$ .

par As(1) qui partage trois de ses sommets: O(3) et O(4) avec deux Ag à la même côte et O(2) avec un Cu et un Ag à une côte différente de celle des deux premiers. Pour As(2), il partage également trois de ses sommets: O(8) avec un Ag, O(7) avec le dimère de Cu et un Ag à

la même côte que le précédent, enfin O(5) avec un Ag qui serait à une côte différente de celle des deux précédents. Les liaisons hydrogène renforceraient encore plus l'édifice. Ceci confère à ce composé sa très grande stabilité.

### Conclusion

Dans le système  $\text{Ag}_2\text{O}-M^{II}\text{O}-\text{As}_2\text{O}_5-\text{H}_2\text{O}$  ( $M^{II}$ : élément de transition) signalons la présence des composés  $M_3^{II}\text{AgH}_2(\text{AsO}_4)_3$  avec  $M^{II} = \text{Co}$  et  $\text{Zn}$  étudiés par Riffel, Zettler & Hess (1979).

### Références

- BOUDJADA, A. (1982a). *Z. Anorg. Allg. Chem.* A paraître.  
 BOUDJADA, A. (1982b). *Mater. Res. Bull.* A paraître.  
 FEHLMANN, M., GHOSE, S. & FINNEY, J. J. (1964). *J. Chem. Phys.* **41**(7), 1910–1916.  
 GHOSE, S. (1963). *Acta Cryst.* **16**, 124–128.  
 GHOSE, S., FEHLMANN, M. & SUNDARALINGAM, M. (1965). *Acta Cryst.* **18**, 777–787.  
 MASSE, R., GUITEL, J. C. & DURIF, A. (1978). *J. Solid State Chem.* **23**, 369–373.  
 RIFFEL, H., ZETTLER, F. & HESS, H. (1979). *Z. Kristallogr.* **149**, 143–144.

*Acta Cryst.* (1982). **B38**, 713–719

## The Structure of the High-Temperature Modification of $\text{V}_3\text{O}_5$ at 458 K

BY S.-H. HONG AND S. ÅSBRINK

*Department of Inorganic Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden*

(Received 19 December 1980; accepted 24 September 1981)

### Abstract

High- $\text{V}_3\text{O}_5$  is monoclinic,  $I2/c$ . Unit-cell dimensions at 458 K are:  $a = 9.846(2)$ ,  $b = 5.0268(4)$ ,  $c = 7.009(1)$  Å,  $\beta = 109.536(15)^\circ$ ,  $V = 326.93$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 4.730$  Mg m<sup>-3</sup>,  $\mu(\text{Mo } K\alpha, \lambda = 0.71069$  Å) =  $8.02$  mm<sup>-1</sup>. The structure was determined from X-ray single-crystal data collected at 458 K with a PAILRED diffractometer, equipped with a specially constructed device for non-ambient temperatures, using the gas-stream technique. The number of symmetry-independent reflexions with observable intensity was 1361, and the number of observations/variables was 33. The least-squares refinement ended with  $R = 0.0257$ ,  $R_w = 0.0333$ . The accuracy of the structure determination is:  $\sigma_{\text{V-V}} = 0.0002\text{--}0.0007$  Å,  $\sigma_{\text{V-O}} = 0.0004\text{--}0.0008$  Å and  $\sigma_{\text{O-O}} = 0.0007\text{--}0.0013$  Å.

0567-7408/82/030713-07\$01.00

High- $\text{V}_3\text{O}_5$ , like low- $\text{V}_3\text{O}_5$ , has a shear structure derived from the rutile structure by crystallographic shear ( $1\bar{2}1$ ). There is a partial separation of tri- and tetravalent vanadium in high- $\text{V}_3\text{O}_5$ , and the tetravalent atoms strongly prefer the position *at* the shear planes. The structure is compared with that of low- $\text{V}_3\text{O}_5$ .

### Introduction

The occurrence of a phase transition above room temperature in the mixed-valency oxide  $\text{V}_3\text{O}_5$  was discovered by Terukov & Chudnovskii (1974) in a study of the optical reflectivity and electrical conductivity of  $\text{V}_3\text{O}_5$  as functions of temperature. They found a semiconductor–semiconductor transition between 423 and 433 K. Its existence was confirmed by

© 1982 International Union of Crystallography

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). In a recent article Chudnovskii, Terukov & Khomskii (1978) state that the transition is of semiconductor-metal type, even though the high-temperature phase is only 'a poor metal'.

The crystal structure of low  $V_3O_5$ , monoclinic with space group  $P2_1/c$ , has been accurately determined at 298 K from single-crystal X-ray diffractometer data (Åsbrink, 1980). To investigate the effect of the phase transformation on the crystal structure, a single-crystal X-ray diffractometer study at 458 K was undertaken.

### Experimental

From a large crystal of  $V_3O_5$ , kindly supplied by Professor Kachi, Department of Chemistry, University of Kyoto, Japan, and prepared by the chemical-transport technique with  $TeCl_4$  as a transport agent (Nagasawa, 1971), an approximately cubic piece was cut (edge  $\sim 0.17$  mm, volume  $\sim 4.7 \times 10^{-3}$  mm<sup>3</sup>). A crystal of larger size than normally used (edge  $< 0.10$  mm) was intentionally chosen to obtain a satisfactory counting accuracy for weak reflexions and a sufficient number of observable reflexions. Data concerning the intensity collection and reduction are given in Table 1.

When the ascending temperature of the specimen passed the phase-transition temperature 427.9 K (Hong & Åsbrink, 1978, 1981) certain critical phenomena were observed, which have been described elsewhere (Åsbrink & Hong, 1979). The high-temperature modification was investigated at  $458 \pm 1$  K, *i.e.* 30 K above the phase-transition point. The determination of the unit-cell parameters is discussed below. The monoclinic symmetry is retained in the transformation, and the unit-cell dimensions change only slightly. It should be noted that the unit-cell volume at 458 K is 0.21% less than at 298 K, a fact which is discussed below.

The determination of the unit-cell parameters was performed on a PAILRED diffractometer with the single crystal used for the complete intensity-data collection. The reciprocal-lattice parameters were determined by measuring the crystal rotation angle  $\omega$  ( $\omega$ -scan mode,  $\omega$  readability 0.001°), in preference to the detector position  $2\theta$ , in order to eliminate some of the error sources: crystal eccentricity, absorption and the detector zero point (Bond, 1960). A remaining source of error was the varying separation of  $K\alpha_1$  and  $K\alpha_2$  reflexions. The use of only completely separated reflexions was impossible, because their number was very small and their intensity generally very weak at an elevated temperature (458 K).

Table 1. *Details of intensity collection and reduction*

Single-crystal diffractometer: PAILRED (inclination geometry), in equi-inclination setting,  $(-\mu)_{\max} \sim 42^\circ$ , equipped with a device for generating non-ambient temperatures (Hong & Åsbrink, 1978, 1981).  
 Monochromatization: graphite crystal, (002) plane,  $\theta_M = 6.08^\circ$ .  
 Diameter of primary-beam tunnel: 1 mm.  
 Scintillation detector, NaI(Tl), with p.h.d.: max. intensity variation over  $5^\circ$  window  $\sim 1\%$ ;  $3^\circ$  window used.  
 Crystal fixed on silica capillary: high-temperature glue (Araldite: X 183/2315, hardener X 157/2316; usable up to  $\sim 520$  K; Ciba-Geigy). X-ray amorphous.  
 Crystal rotation axes: [010] (main measurements,  $k \leq 9$ ), [001] (complementary measurements:  $h, 10, l, 0k0$ ).  
 Scan mode:  $\omega$  scan. Scan speed (deg min<sup>-1</sup>): 1.  
 $2\theta$  interval ( $^\circ$ ): 0–100.  
 Number of measured unique reflexions: 3755.  
 Number of possible non-extinct unique reflexions: 1724.  
 Number of observable unique reflexions [ $I_o > 2.5\sigma(I_o)$ ]: 1361.  
 Some 80 reflexions with highest peak intensity remeasured with lower X-ray tube power to avoid counting losses.  
 Transformation of raw result to  $L_p$ -corrected net intensities [programs by Brandt (1971)]; monochromator crystal assumed to behave as an ideally mosaic crystal (*N.b.*  $\theta_M = 6.08^\circ$ ).  
 Absorption correction by numerical integration method [program by Coppens, Leiserowitz & Rabinovich (1965)] including preparatory calculations for secondary-extinction corrections [(Zachariasen, 1967); modification for inclination geometry by Åsbrink (1973, unpublished)]; mass absorption coefficients from *International Tables for X-ray Crystallography* (1974), 1000 integration elements; range of transmission factor: 0.317–0.377.

Consequently, the main difficulty in the present case was to locate a reflexion accurately. A frequently used method is to allocate half-peak intensity positions. However, this method is also somewhat inaccurate. The determination of the upper-half-peak intensity position (larger  $\omega$ ) is always difficult, because the intensity ratio of  $K\alpha_1$  and  $K\alpha_2$  is just 2:1, which makes the upper-half-peak intensity position very sensitive to diffraction angle. The ambiguity in the determination of the upper-half-peak intensity position generally increases with  $2\theta$ ; it was sometimes as large as  $0.1^\circ$ , and may be even larger.

Therefore we applied a method to locate a reflexion by means of its 'feet'. One can assume that the lower- and higher-angle feet of a reflexion, corresponding to crystal rotations  $\omega_1$  and  $\omega_2$ , are exclusively contributed to by the  $K\alpha_1$  and  $K\alpha_2$  beams, respectively, at  $2\theta \gtrsim 10^\circ$ .  $\omega_1$  and  $\omega_2$  were determined as the  $\omega$  values where  $I = \bar{B}_1 + 2\sigma(I_p)$  and  $\bar{B}_2 + 2\sigma(I_p)$ , respectively.  $\bar{B}_1$  and  $\bar{B}_2$  are average background counts for one minute (c.p.m.) at  $\omega_1$  and  $\omega_2$  respectively, and  $\sigma(I_p) = \sqrt{I_p}$ ,  $I_p$  being the peak intensity (c.p.m.). Thus, a middle point  $\omega_m$ ,  $\frac{1}{2}(\omega_1 + \omega_2)$ , of the crystal rotation angle value for a reflexion was obtained [quantities other than  $\bar{B}_i + 2\sigma(I_p)$  for the allocation of  $\omega_1$  and  $\omega_2$  are discussed in the deposited material].\* The accuracy of the measured  $\omega_m$  was much higher than that given

\* See following footnote.

by the method of the half-peak intensity positions, and the typical deviation was less than  $0.02^\circ$ .

One obtains  $a^*$  by plotting  $\omega_m - \arcsin(hA/2)$  versus  $A$  (r.l.u. =  $\lambda_m/d$ ; Hornstra, 1965) for a set of  $h00$  reflexions. For example  $a_1^*$  was obtained from six  $h00$  reflexions as an average value of  $A$  for the 15 intersections of the six straight lines. Analogously,  $a_2^*$  was obtained from six  $\bar{h}00$  reflexions. The final  $a^*$  value was obtained as the average of  $a_1^*$  and  $a_2^*$ . The values of  $a^*$ ,  $b^*$  and  $c^*$  obtained in this manner do not correspond to the intensity-weighted average wavelength  $\lambda$ ,  $0.71069 \text{ \AA}$ , for Mo  $K\alpha$ , but a simple mean wavelength  $\lambda_m$ ,  $0.71140 \text{ \AA}$  (*International Tables for X-ray Crystallography*, 1968).

The validity of the combination of  $\omega_m$  and  $\lambda_m$  was checked by determining the unit-cell parameters of low- $V_3O_5$  (298 K) and comparing them with those (Åsbrink, 1980) obtained from a powder diffraction film exposed in a Guinier-Hägg focusing camera with Cu  $K\alpha_1$  radiation (quartz monochromator). The unit-cell parameters obtained in the two different ways were coincident within the experimental errors ( $\sim 2\sigma$ ).

The presented allocation method is most successful with the combination of a graphite monochromator and a pulse-height analyser, because such a combination yields a broad homogeneous incident beam with a nearly 1 mm broad plateau at the sample crystal and, accordingly, a very symmetrical and very low background (a detailed description of the allocation method is given in the deposited material).

### Structure determination

The reflexions  $hkl$  with observable intensity in high- $V_3O_5$  all have  $h + k + l = 2n$ , i.e. all the very weak

reflexions of low- $V_3O_5$  characterized by  $h + k + l = 2n + 1$  disappear in the phase transformation at  $427.9 \text{ K}$ . Furthermore,  $h0l$  are observed only with  $l = 2n$  ( $h = 2n$ ), indicating space group  $I2/c$  (No. 15) or  $Ic$  (No. 9). Low- $V_3O_5$  has space group  $P2/c$ . As it seemed unlikely that the crystal structure would lose its centre of symmetry in a phase transformation at an increased temperature,  $I2/c$  was tested, this choice later proving to be correct. As this was also the space group of the idealized  $V_3O_5$ -structure (Åsbrink in the report by Magnéli, Andersson, Westman, Kihlberg, Holmberg, Åsbrink & Nordmark, 1959) atomic coordinates for this structure were taken as starting parameters for least-squares calculations (after taking into proper consideration a new choice of unit cell). In these calculations, carried out with the program *FALFA* (Koenig, 1971, unpublished), 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. Data on the calculations are given in Table 2. The final atomic coordinates and equivalent isotropic thermal parameters  $B_{eq}$  (Hamilton, 1959) are presented in Table 3. The final value of the isotropic secondary-extinction-correction variable was  $5.5(1) \times 10^4$ . A successful secondary-extinction correction has a decisive significance for the accurate structure determination, because 25% (342 reflexions) of the observed unique reflexions (1361) had  $y < 0.90$  ( $y = I_o/I_c$ ; Zachariasen, 1967).

Interatomic distances calculated with program *DISTAN* (A. Zalkin, Berkeley, California, USA; local version by A. G. Nord & B. G. Brandt) are given in Table 4, where also a comparison is made with the

Table 2. *Structure refinement*

The final refinement (cf. Table 3): The suitability of the weighting function used was tested by weight analyses (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961). No parameter shift larger than  $0.01\sigma$  in the last cycle. Only ten correlation coefficients of 820 had absolute values  $> 0.50$ , the largest being 0.82. A final  $F_c$  calculation for the unobserved reflexions showed all  $|F_c|$  to be satisfactorily small.

	Number of refined parameters, $n$	Number of reflexions, $m$	$R = \frac{\sum  A^* }{\sum  F_o }$	$R_w = \frac{\sum wA^2}{\sum wF_o^2}^{1/2}$	$S = [\sum wA^2/(m-n)]^{1/2}$	$w^{-1}$
16	10 atomic coordinates, 5 $B$ ( $\text{\AA}^2$ ), 1 scale factor	1361	0.090	0.114	12.77	$\sigma^2(F_o)$
41	10 atomic coordinates, 28 $\beta_{ij}$ 2 scale factors, 1 secondary extinction	1361	0.025	0.026	2.973	$\sigma^2(F_o)$
41	10 atomic coordinates, 28 $\beta_{ij}$ 2 scale factors, 1 secondary extinction	1361	0.0257	0.0333	1.377	$\sigma^2(F_o) + 5 \times 10^{-5} \times F_o^2 + 10^{-6} \times  F_o ^3$

$$* A = |F_o| - |F_c|.$$

corresponding distances in low- $V_3O_5$  (Åsbrink, 1980). Figs. 1, 2, 3 and 4 were obtained by the use of program

Table 3. Positional parameters ( $\times 10^6$  for vanadium,  $\times 10^5$  for oxygen) and equivalent isotropic thermal parameters  $B_{eq}$  ( $\times 10^3$ , Hamilton, 1959)

Numbers in parentheses are e.s.d.'s in the last significant digits. Space group  $I2/c$  (No. 15 in an alternative orientation): coordinates of equivalent positions  $8(f)$ ,  $4(e)$  and  $4(b)$  are  $(0,0,0; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \pm (x, y, z; x, \bar{y}, \frac{1}{2} + z)$ ,  $\pm(0, y, \frac{1}{4})$  and  $\pm(0, \frac{1}{2}, 0; 0, \frac{1}{2}, \frac{1}{4})$ , respectively.

		$x$	$y$	$z$	$B_{eq}$ ( $\text{\AA}^2$ )
V(1)	8(f)	370346 (13)	498405 (19)	89850 (19)	475 (3)
V(2)	4(b)	0	$\frac{1}{4}$	0	459 (4)
O(1)	8(f)	69257 (7)	84750 (12)	53331 (10)	731 (11)
O(2)	8(f)	58100 (7)	34401 (10)	63796 (9)	531 (9)
O(3)	4(e)	0	30642 (14)	$\frac{1}{4}$	570 (13)

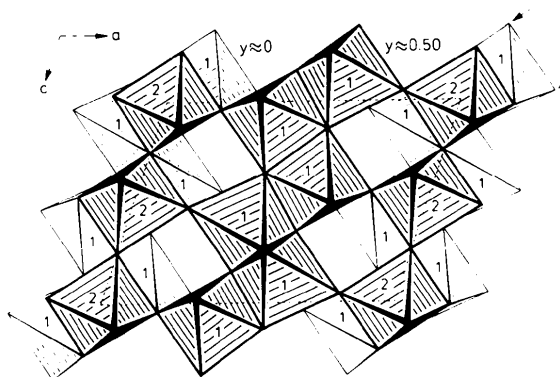


Fig. 1. The coupling of octahedra in high- $V_3O_5$ . [010] projection of two layers of octahedra ( $y \sim 0$  and  $y \sim 0.5$ , respectively). Numbers 1 and 2 denote V(1)-O and V(2)-O octahedra, respectively. The arrows limit a section which is presented in Fig. 2.

Table 4. Interatomic distances ( $\text{\AA}$ ): a comparison between low- $V_3O_5$  (298 K) and high- $V_3O_5$  (458 K)

$e$  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 irregularity of the octahedron (see text). Further numbers in parentheses are e.s.d.'s in the least significant digits.

		298 K		458 K	
V(11)-O(11)	1.7240 (8)	V(12)-O(12)	1.8912 (8)	V(1)-O(1)	1.8255 (8)
-O(12)	1.9240 (9)	-O(11)	2.0270 (10)	-O(1)	1.9623 (6)
-O(21)	1.9638 (9)	-O(22)	1.9756 (9)	-O(2)	1.9711 (7)
-O(21)	1.9650 (9)	-O(22)	1.9806 (9)	-O(2)	1.9731 (6)
-O(31)	2.0336 (9)	-O(32)	2.0913 (10)	-O(3)	2.0686 (6)
-O(21)	2.1734 (8)	-O(22)	2.1316 (8)	-O(2)	2.1390 (7)
Average	1.9640		2.0162		1.9899
	(1.9337)		(2.0060)		(1.9744)
O(21)-O(21) $e$	2.578 (2)	O(22)-O(22) $e$	2.579 (2)	O(2)-O(2) $e$	2.5848 (12)
O(21)-O(21) $f$	2.585 (2)	O(22)-O(22) $f$	2.566 (2)	O(2)-O(2) $f$	2.5858 (13)
O(21)-O(31) $f \times 2$	2.607 (2)	O(22)-O(32) $f \times 2$	2.711 (2)	O(2)-O(3) $f \times 2$	2.6598 (8)
O(21)-O(31) $e$	2.670 (1)	O(22)-O(32) $e$	2.670 (1)	O(2)-O(3) $e$	2.6743 (7)
O(21)-O(12) $e$	2.686 (1)	O(22)-O(11) $e$	2.789 (1)	O(2)-O(1) $e$	2.7314 (10)
O(21)-O(12)	2.725 (2)	O(22)-O(11)	2.833 (1)	O(2)-O(1)	2.7886 (10)
O(11)-O(12)	2.797 (2)	O(12)-O(11)	2.908 (2)	O(1)-O(1)	2.8579 (7)
O(21)-O(11)	2.815 (1)	O(22)-O(12)	2.897 (1)	O(2)-O(1)	2.8639 (10)
O(21)-O(12)	2.895 (2)	O(22)-O(11)	3.016 (2)	O(2)-O(1)	2.9477 (8)
O(11)-O(31)	2.930 (1)	O(12)-O(32)	3.062 (1)	O(1)-O(3)	2.9989 (9)
O(21)-O(11)	2.957 (1)	O(22)-O(12)	3.137 (1)	O(2)-O(1)	3.0411 (10)
Average	2.738		2.823		2.7828
V(21)-O(12) $\times 2$	1.9609 (8)	V(22)-O(11) $\times 2$	2.0414 (8)	V(2)-O(1) $\times 2$	1.9852 (8)
-O(31) $\times 2$	2.0249 (7)	-O(32) $\times 2$	1.9815 (7)	-O(3) $\times 2$	2.0043 (4)
-O(21) $\times 2$	2.0392 (9)	-O(22) $\times 2$	1.9954 (9)	-O(2) $\times 2$	2.0114 (6)
Average	2.0083		2.0061		2.0003
	(2.0064)		(2.0051)		(2.0001)
O(21)-O(31) $e \times 2$	2.670 (1)	O(22)-O(32) $e \times 2$	2.670 (1)	O(2)-O(3) $e \times 2$	2.6743 (7)
O(21)-O(12) $e \times 2$	2.686 (1)	O(22)-O(11) $e \times 2$	2.789 (1)	O(2)-O(1) $e \times 2$	2.7314 (10)
O(12)-O(31) $\times 2$	2.793 (1)	O(11)-O(32) $\times 2$	2.842 (1)	O(1)-O(3) $\times 2$	2.8053 (8)
O(12)-O(31) $\times 2$	2.844 (1)	O(11)-O(32) $\times 2$	2.848 (1)	O(1)-O(3) $\times 2$	2.8366 (9)
O(12)-O(21) $\times 2$	2.965 (2)	O(11)-O(22) $\times 2$	2.919 (2)	O(1)-O(2) $\times 2$	2.9177 (8)
O(21)-O(31) $\times 2$	3.064 (2)	O(22)-O(32) $\times 2$	2.948 (2)	O(2)-O(3) $\times 2$	2.9957 (9)
Average	2.837		2.836		2.8268
V(11)-V(11) $f$	2.8171 (4)	V(12)-V(12) $f$	2.7632 (4)	V(1)-V(1) $f$	2.7794 (7)
V(11)-V(21) $e$	2.9708 (3)	V(12)-V(22) $e$	2.9730 (3)	V(1)-V(2) $e$	2.9734 (2)
V(11)-V(21) $e$	3.0239 (3)	V(12)-V(22) $e$	3.0020 (3)	V(1)-V(2) $e$	2.9869 (2)
V(11)-V(11) $e$	3.2438 (4)	V(12)-V(12) $e$	3.2067 (4)	V(1)-V(1) $e$	3.2025 (6)

ORTEP (Johnson, 1965; local version by I. Carlborn & A. G. Nord).\*

\* Lists of structure factors and anisotropic thermal parameters and an expanded description of the reflexion-allocation procedure have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36430 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

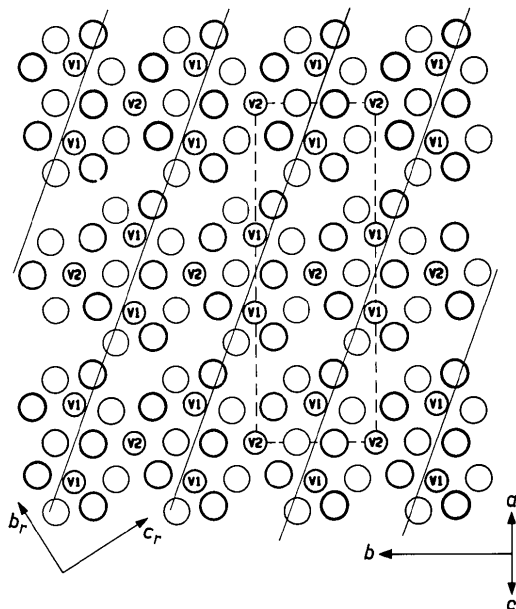


Fig. 2. A projection on (101) of the section between the arrows in Fig. 1 showing the hexagonal close packing of O atoms in  $V_3O_5$  and the relation between the rutile and  $V_3O_5$  structures. The axes of the rutile subcell are denoted  $b_r$  and  $c_r$ , respectively. Empty circles indicate O atoms, and circles marked with V1 and V2 indicate vanadium positions V(1) and V(2), respectively, in the high- $V_3O_5$  structure. The full lines indicate the intersections of the slanting shear planes with (101) at  $x + z = 1$ .

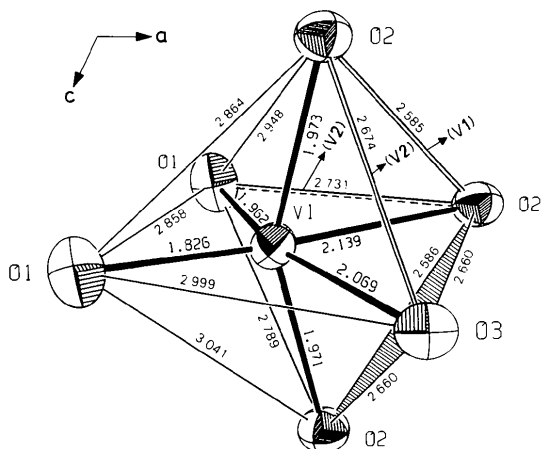


Fig. 3. Vanadium atom V(1) with oxygen coordination octahedron. The face in common with an octahedron around another V(1) atom is shaded. Edges shared with other octahedra are indicated by double lines (95% probability ellipsoids). (Distances in Å.)

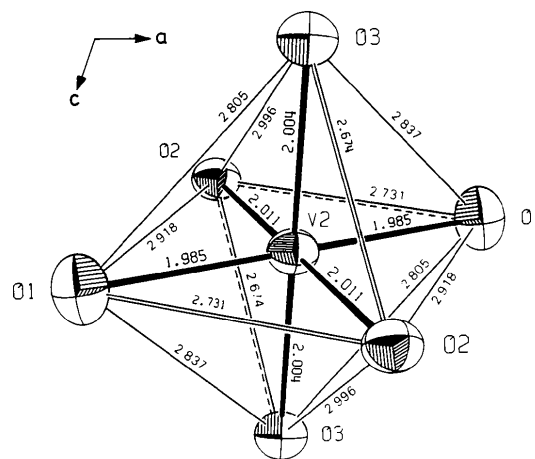


Fig. 4. Vanadium atom V(2) with oxygen coordination octahedron. Edges shared with other octahedra, all containing V(1) atoms, are indicated by double lines (95% probability ellipsoids). (Distances in Å.)

## Discussion

The crystal structure of high- $V_3O_5$ , as well as of low- $V_3O_5$ , can be described as a hexagonal close packing of O atoms with the octahedral interstices partially filled with V 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. 1). 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, Tokonami, Morimoto, Nagasawa, Bando & Takada (1971) have pointed out that  $V_3O_5$  may be considered as a member of the homologous series  $V_nO_{2n-1}$  derived from the rutile structure by crystallographic shear (121). With this view, the eightfold vanadium position V(1) in the double-octahedral chains of high- $V_3O_5$  is situated *at* the shear planes, while the fourfold position V(2) in the single-octahedral chains is situated *between* the shear planes (*cf.* Fig. 2).

The interatomic distances in high- $V_3O_5$  are presented in Table 4 together with the corresponding distances in low- $V_3O_5$  (Åsbrink, 1980). By comparing average V—O as well as O—O distances one concludes that the two independent V—O octahedra in high- $V_3O_5$  are less different than are the V(11)—O octahedron, on the one hand, and the remaining three V—O octahedra, on the other hand, in low- $V_3O_5$ . There is a dissimilarity, though, which points to a difference in oxidation number between V(1) and V(2). However, by checking the individual V—O as well as O—O distances one

observes that the centrosymmetric V(2)—O octahedron is far more regular than the V(1)—O octahedron. Thus one cannot simply compare the two  $\overline{V(1)-O}$  and  $\overline{V(2)-O}$  values, for the following reason: if one assumes a logarithmic relation between bond strength and bond length (Pauling, 1947; Zachariassen, 1978) to be approximately correct, one can predict that the average bond length  $\overline{V-O}$  for an octahedron with a V atom of given valency as the central atom should increase as the distortion of the octahedron increases. A correction term to be added to the observed  $\overline{V-O}$  value can be derived from such a 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 Zachariassen (1978), *i.e.*  $d_i = d(1)(1 - 0.171 \ln S_i)$ , where  $d_i$  is the observed bond length (Å),  $S_i$  is the corresponding bond strength and  $d(1)$  is a constant, *viz.* the distance of a bond of unit bond strength, here chosen as 1.8015 Å. The correction term is thus  $-d(1) \times 0.171 \times \ln[\bar{S}/(S_1 S_2 \dots S_6)^{1/6}]$ , with  $\bar{S} = \sum_{i=1}^6 S_i/6$ .

The 'corrected' averages are presented below the uncorrected ones in Table 4. The former differ more than the latter, as expected. Thus, the indication of a valency difference between V(1) and V(2) is strengthened. Bond-strength calculations using Zachariassen's (1978) equation with  $d(1) = 1.8015$  Å gave the valencies (= bond-strength sums) 3.42 and 3.15 for V(1) and V(2), respectively. The valency sum for the whole unit cell became 39.98, which is satisfactorily close to the ideal value of 40. In low- $V_3O_5$  at 298 K there is strong evidence for a complete separation of  $V^{III}$  and  $V^{IV}$  (Åsbrink, 1980), such that position V(11) contains  $V^{IV}$ , and positions V(12), V(21) and V(22) all contain  $V^{III}$ . In the phase transformation V(11) and V(12), and V(21) and V(22) of low- $V_3O_5$  coalesce into V(1) and V(2), respectively, of high- $V_3O_5$ . V(1) might therefore contain a 50:50 mixture of  $V^{III}$  and  $V^{IV}$ , and V(2),  $V^{III}$ . This would lead to the ideal bond-strength sums 3.50 and 3.00, respectively. The derived bond-strength sums, 3.42 and 3.15, point to a somewhat more disordered valency distribution. It might be that just above the phase-transformation temperature the distribution is the more ordered one suggested above. Anyhow, the preference of  $V^{IV}$  for the sites *at* the shear planes is still very strong at 458 K.

As the bond-strength sums above were derived from bond distances uncorrected for the effect of the rather large thermal vibrations of the atoms, it was investigated whether such corrections would significantly change the result of the valency discussion. The mathematical models available, 'riding motion' and 'independent motion', were tested (ORFFE, Busing, Martin & Levy, 1964). The changes in the derived

bond-strength sums appeared in or beyond the third decimal place. However unrealistic the applied models may be in the present case, the result suggests that the validity of the valency discussion is not reduced by the lack of a relevant method for thermal-motion correction of the bond distances.

The  $d(1)$  value used in high- $V_3O_5$ , 1.8015 Å, is larger than that used in low- $V_3O_5$ , 1.799 Å. This is reasonable, as an increased temperature should lengthen the distance of a bond of given strength,  $S$ . As mentioned, the unit-cell volume of high- $V_3O_5$  is smaller than that of low- $V_3O_5$ , a fact which, at first, may seem astonishing. In low- $V_3O_5$  the grand-average V—O bond length, 1.9958 Å, calculated over the whole unit cell, is larger than the corresponding quantity in high- $V_3O_5$ , 1.9934 Å, in spite of the lower temperature of 160 K at which low- $V_3O_5$  was studied. This is in qualitative agreement with the observed change of the cell volume. However, after application of the irregularity correction the grand-averages revert to a more natural order, *viz.* 1.9818 and 1.9830 Å for low- and high- $V_3O_5$ , respectively. The conclusion is that the unit-cell volume of low- $V_3O_5$  is larger than that of high- $V_3O_5$  because of the more distorted coordination octahedra in low-compared to high- $V_3O_5$ .

It seems as if accurate single-crystal investigations at different temperatures of the same crystal would be of value for investigations of the parameters of the logarithmic relation, or even for testing the logarithmic relation *per se*. The reasonableness of the changes of  $d(1)$  with temperature, for example, could be tested by such investigations in combination with accurate determinations of the expansion coefficients.

By considering the individual V—O bonds in high- $V_3O_5$  one finds that in the non-centrosymmetric octahedron the shortest V(1)—O bond engages the only O atom which belongs neither to a shared face nor to a shared edge of the V(1)—O octahedron. The longest V(1)—O bond, on the other hand, connects vanadium to the O atom which is engaged in the largest number of edge and face sharings (*cf.* Fig. 3). Analogous observations can be made for low- $V_3O_5$  (Åsbrink, 1980), and they might be explained mainly as effects of repulsions between V atoms.

The V—V distances in high- $V_3O_5$  are very similar to the corresponding distances in low- $V_3O_5$  (Table 4). Thus, the phase transformation of  $V_3O_5$  does not introduce any apparent change in the metal—metal interaction, either across a shared octahedral face or across a shared edge [*cf.* the diminutive change in the magnetic susceptibility at the transformation, according to Brückner *et al.* (1975) and Sävborg (1980)]. In this connexion comparison may be made with the insulator—metal transformations in the single-valency vanadium oxides  $V_2O_3$  and  $VO_2$ . Their crystal structures are related to those of  $V_3O_5$ , the common feature being the more or less ideal hexagonal close packing of

the O atoms. Both the transformation in  $V_2O_3$  and that in  $VO_2$  involve much larger and more clear-cut changes: In the transformation  $V_2O_3$  (insulator)  $\rightarrow$   $V_2O_3$  (metal) at room temperature, the insulator phase being Cr-doped,  $V-V_f$  (*cf.* Table 4) changes from 2.746 to 2.697 Å and  $V-V_e$  (*cf.* Table 4) from 2.918 to 2.882 Å (Dernier, 1970). In  $VO_2$ , the  $V-V_e$  distance in  $VO_2$  (insulator) at room temperature is 2.619 Å (Longo & Kierkegaard, 1970), and the corresponding distance in  $VO_2$  (metal) at 470 K is 2.860 Å (McWhan, Marezio, Remeika & Dernier, 1974). The evident lack of a  $V-V$  bond across a shared octahedral edge in either modification of  $V_3O_5$ , in contrast to the simple oxides, may be correlated with the fact that in low- as well as in high- $V_3O_5$ , the shortest  $V-V$  contacts, where a bond might be established, are between V atoms of different valency (*cf.* Table 4).

We are grateful to Professors Arne Magnéli and Peder Kierkegaard for their kind interest and for the excellent facilities put at our disposal. We are indebted to Professor Sukeji Kachi who supplied the crystals of  $V_3O_5$  and to Dr Sven Westman for correcting the English of the paper.

This work has been supported by a grant from the Swedish Natural Science Research Council.

#### References

- ALLMANN, R. (1975). *Monatsh. Chem.* **106**, 779–793.  
 ÅSBRINK, S. (1975). *Mater. Res. Bull.* **10**, 861–864.  
 ÅSBRINK, S. (1980). *Acta Cryst.* **B36**, 1332–1339.  
 ÅSBRINK, S. & HONG, S.-H. (1979). *Nature (London)*, **279**, 624–625.  
 BOND, W. L. (1960). *Acta Cryst.* **13**, 814–818.  
 BRANDT, B. G. (1971). *Chem. Commun. Univ. Stockholm*, No. II.  
 BRÜCKNER, W., MOLDENHAUER, W., THUSS, B. & FÖRSTERLING, G. (1976). *Phys. Status Solidi A*, **35**, K49–K51.  
 BRÜCKNER, W., WICH, H., TERUKOV, E. I. & CHUDNOVSKII, F. A. (1975). *Fiz. Tverd. Tela (Leningrad)*, **17**, 2191–2193.  
 BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Report ORNL-TM-306. Oak Ridge National Laboratory, Tennessee.  
 CHUDNOVSKII, F. A., TERUKOV, E. I. & KHOMSKII, D. I. (1978). *Solid State Commun.* **25**, 573–577.  
 COPPENS, P., LEISEROWITZ, L. & RABINOVICH, D. (1965). *Acta Cryst.* **18**, 1035–1038.  
 CRUICKSHANK, D. W. J., PILLING, D. E., BUJOSA, A., LOVELL, F. M. & TRUTER, M. R. (1961). *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, p. 45. Oxford: Pergamon Press.  
 DERNIER, P. D. (1970). *J. Phys. Chem. Solids*, **31**, 2569–2575.  
 HAMILTON, W. C. (1959). *Acta Cryst.* **12**, 609–610.  
 HONG, S.-H. & ÅSBRINK, S. (1977). 4th Eur. Crystallogr. Meet. Oxford, PII. 85.  
 HONG, S.-H. & ÅSBRINK, S. (1978). *Acta Cryst.* **A34**, S344.  
 HONG, S.-H. & ÅSBRINK, S. (1981). *J. Appl. Cryst.* **14**, 43–50.  
 HORIUCHI, H., TOKONAMI, M., MORIMOTO, N., NAGASAWA, K., BANDO, Y. & TAKADA, T. (1971). *Mater. Res. Bull.* **6**, 833–843.  
 HORNSTRA, J. (1965). Natl Lab. Rep. 4021. Philips Research Laboratories, Eindhoven.  
*International Tables for X-ray Crystallography* (1968). Vol. III. Birmingham: Kynoch Press.  
*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.  
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.  
 KARTENKO, N. F., TERUKOV, E. I. & CHUDNOVSKII, F. A. (1976). *Fiz. Tverd. Tela (Leningrad)*, **18**, 1874–1876.  
 LONGO, J. M. & KIERKEGAARD, P. (1970). *Acta Chem. Scand.* **24**, 420–426.  
 MCWHAN, D. B., MAREZIO, M., REMEIKA, J. P. & DERNIER, P. D. (1974). *Phys. Rev. B*, **10**, 490–495.  
 MAGNÉLI, A., ANDERSSON, S., WESTMAN, S., KIHLBORG, L., HOLMBERG, B., ÅSBRINK, S. & NORDMARK, C. (1959). *Studies on the Crystal Chemistry of Titanium, Vanadium and Molybdenum Oxides at Elevated Temperatures. Final Technical Report 1*, DA-91-591-EUC-935, pp. 23–30.  
 NAGASAWA, K. (1971). *Mater. Res. Bull.* **6**, 853–864.  
 PAULING, L. (1947). *J. Am. Chem. Soc.* **69**, 542–553.  
 SÄVBORG, Ö. (1980). *Mater. Res. Bull.* **15**, 171–176.  
 TERUKOV, E. I. & CHUDNOVSKII, F. A. (1974). *Fiz. Tekh. Poluprovodn.* **8**, 1226–1227.  
 ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.  
 ZACHARIASEN, W. H. (1978). *Acta Cryst.* **A34**, S406.