

Fig. 2. Orthogonal projection of the atomic arrangement of  $\text{As}_2\text{V}_4\text{O}_{13}$  on the (010) plane ( $y$  atomic coordinates  $\times 10^2$ ).

The  $\text{VO}_6$  octahedra sharing edges and corners build up as two chains along the [010] direction sharing corners and held together by  $\text{AsO}_4$  tetrahedra. The distribution of the cations  $\text{As}^{5+}$  and  $\text{V}^{4+}$  within the network of oxygen atoms forming cubic close packing is complicated.

We have started the investigation of the glassy architecture of the 'AsVO' system using the knowledge

of the structure of  $\text{As}_2\text{V}_4\text{O}_{13}$  and the assumptions by Galy, Meunier, Andersson & Åström (1975) and Galy & Enjalbert (1982) that the lone pairs in  $\text{AsO}_3\text{E}$  may be substituted by  $\text{AsO}_4$  or  $\text{VO}_4$  tetrahedra in oxide networks.

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## A Refinement of the Structure of $\text{V}_2\text{O}_5$

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**Abstract.** Vanadium pentoxide,  $M_r = 181.88$ , orthorhombic,  $Pm\bar{m}n$ ,  $a = 11.512(3)$ ,  $b = 3.564(1)$ ,  $c = 4.368(1)$  Å,  $V = 179.2(1)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 3.37$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) = 0.71069$  Å,  $\mu = 4.94$  mm<sup>-1</sup>,  $F(000) = 172$ ,  $T = 292$  K,  $R = 0.020$ ,  $wR = 0.027$  for 334 unique reflections collected up to  $\theta = 36^\circ$  and 24 variable parameters.  $\text{V}_2\text{O}_5$ , a layered structure, built up

from  $\text{VO}_5$  square pyramids sharing edges and corners, with  $\text{V}_2\text{O}_5$  sheets held together *via* weak vanadium–oxygen interaction,  $\text{V}–\text{O} = 2.791(3)$  Å. The structural investigation is confirmed and made more precise, showing a slight difference in the description of  $\text{VO}_5$  polyhedra (square pyramid instead of trigonal bipyramid).

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**Introduction.**  $V_2O_5$  is an important fundamental oxide both for its chemical (especially in catalysis) and physical properties. The first investigation of its orthorhombic structure was performed by Ketelaar (1936). Dissatisfied by some aspects of the crystal structure, Byström, Wilhelmi & Brotzen (1950) have proposed in this orthorhombic network, space group  $Pmmn$ , a new structural description based on trigonal bipyramids sharing edges and corners, making  $V_2O_5$  sheets. Later, Bachmann, Ahmed & Barnes (1961) confirmed this work, without any significant discrepancies.

In the course of our investigations by insertion of molecular complexes into the slabs of  $V_2O_5$ , structural information based on accurate data collection and full-matrix least-squares refinement was needed to render more precise the network coordination mode of V atoms. In previous investigations, data were obtained from Weissenberg photographs using  $Cu K\alpha$  radiation and corrected empirically for absorption ( $R$  factors: 0.10 and 0.14) (Byström *et al.*, 1950); or for  $Mo K\alpha$  radiation using a single crystal oriented for an X-ray spectrogoniometer and approximately corrected for absorption (Bachmann *et al.*, 1961). It was possible to obtain an improved data set and the refinement of the crystal structure of  $V_2O_5$  was then undertaken.

**Experimental.** Crystals obtained from melting a mixture of  $V_2O_5$  and  $As_2O_3$  at 873 K in the ratio 4:1; orange-yellow prismatic crystals, {100}, {010} and {001} boundary faces, dimensions 0.050 × 0.025 × 0.125 mm; cell dimensions from least-squares fit to 25 reflections measured in the range  $5 \leq \theta \leq 30^\circ$ ; Enraf-Nonius CAD-4 diffractometer; graphite-monochromatized  $Mo K\alpha$  radiation; maximum Bragg angle:  $\theta_{max} = 36^\circ$ ; take-off angle:  $2.6^\circ$ ;  $\theta-2\theta$  scan mode;  $\Delta\theta = 0.75^\circ + 0.35^\circ \tan\theta$ ; prescan speed:  $10^\circ \text{ min}^{-1}$ ;  $\sigma(I)/I$  for final scan: 0.018; max. time for final scan: 80 s; standard reflections: 310, 600, 620; no significant variation; 450 unique reflections measured; range of  $hkl$ :  $h0 \rightarrow 19$ ,  $k0 \rightarrow 5$ ,  $l0 \rightarrow 7$ ; Lorentz-polarization factor; numeric absorption correction; transmission coefficient variation: 0.77 → 0.89; 334 reflections with  $I > 3\sigma(I)$  utilized; full-matrix least-squares ( $F$ ); 24 refined variable parameters; extinction coefficient  $g = 4.3 \times 10^{-6}$ ;  $(\Delta/\sigma)_{max} < 0.01$ ; final indices:  $R = 0.020$ ;  $wR = 0.027$ ;  $w = 1$ ;  $S = 0.632$ ; scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); calculations performed with *SDP* (Enraf-Nonius, 1979) on a VAX/730; illustrations with *ORTEPII* (Johnson, 1976). The last difference Fourier map indicates only a small amount of electron density,  $< 0.6 \text{ e } \text{Å}^{-3}$ , at the middle of V-O bonds.

and angles are given in Table 2 with the numbering of the atoms.\*

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43078 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional and thermal parameters (e.s.d.'s in parentheses)*

$$B_{eq} = \frac{4}{3} \sum_i \sum_j (\mathbf{a}_i \cdot \mathbf{a}_j) \beta_{ij}$$

	$x$	$y$	$z$	$B_{eq}(\text{Å}^2)$
V	0.10118 (8)	$\frac{1}{4}$	0.8917 (2)	0.54 (1)
O(1)	0.1043 (4)	$\frac{1}{4}$	0.531 (1)	1.21 (7)
O(2)	-0.0689 (3)	$\frac{1}{4}$	0.003 (1)	0.79 (6)
O(3)	$\frac{1}{4}$	$\frac{1}{4}$	0.001 (2)	0.9 (1)

Table 2. *Selected distances (Å) and angles ( $^\circ$ )*

V(1,1)	O(1,1)	O(3,1)	O(2,3)	O(2,3')	O(2,1)	O(1,1')
O(1,1)	1.577 (3)	2.652 (6)	2.738 (4)	2.738 (4)	2.868 (5)	4.368
O(3,1)	104.3 (2)	1.779 (2)	2.742 (2)	2.742 (2)	3.671 (3)	2.857 (6)
O(2,3)	104.5 (1)	97.1 (1)	1.878 (1)	3.564	2.386 (4)	2.961 (4)
O(2,3')	104.5 (1)	97.1 (1)	143.2 (2)	1.878 (1)	2.386 (4)	2.961 (4)
O(2,1)	105.2 (2)	150.5 (2)	75.5 (1)	75.5 (1)	2.017 (3)	3.050 (5)
O(1,1')	177.9 (2)	73.7 (2)	75.9 (1)	75.9 (1)	76.9 (1)	2.791 (3)

	V(1,2)	V(1,3)
V(1,1)	3.427 (1)	3.082 (1)

	Point set	Label
$4(f)$	$x$	$\frac{1}{4}$ z (n,1)
	$-x + \frac{1}{2}$	$\frac{1}{4}$ z (n,2)
	$-x$	$\frac{1}{4}$ -z (n,3)
	$x + \frac{1}{2}$	$\frac{1}{4}$ -z (n,4)
$2(a)$	$x$	$\frac{1}{4}$ z (n,1)
	$\frac{1}{2}$	$\frac{1}{4}$ z (n,2)
	$\frac{1}{2}$	$\frac{1}{4}$ -z (n,3)
	$\frac{1}{2}$	$\frac{1}{4}$ -z (n,4)

with translation of one period ( $n, m'$ ).

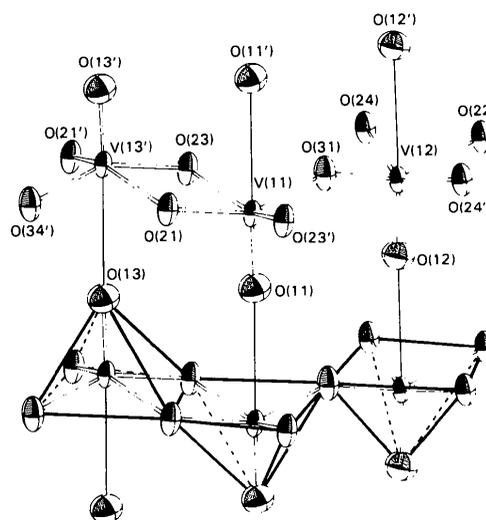


Fig. 1. Chain of corner-sharing octahedra associated with a chain of edge-sharing octahedra (thermal ellipsoids: 90% probability).

**Discussion.** Final positional and isotropic thermal parameters are listed in Table 1. Selected bond lengths

The details of the association of coordination polyhedra around V atoms are shown in Fig. 1. Bond lengths and angles agree well with the Byström *et al.* (1950) and Bachmann *et al.* (1961) structural determinations. Compared with these fundamental models, the present result gives precise anisotropic thermal parameters and settles definitively the short O—O distance observed, 2.386 (4) Å.

The oxygenated coordination polyhedron around the V atoms should be described in terms of a square (SP) instead of a trigonal pyramid (TBP) as indicated by the previous authors. A calculation based on the dihedral angles of the polyhedron as proposed by Galy, Bonnet & Andersson (1979) gives  $\Delta=0.845$  (pure TBP and pure SP give  $\Delta=0$  and 1, respectively) indicating a slight distortion of the square pyramid; it is also to be noticed that the base of  $V_2O_5$ , built up by the oxygen atoms O(21), O(31), O(23), O(23'), is quasi-planar [dihedral angle O(21)O(31)O(23)/O(21)O(31)O(23') is  $1.4^\circ$ ] and the distances of the atoms to the average plane are  $-0.013(4)$ ,  $-0.010(9)$ ,  $0.011(4)$  and  $0.011(4)$  Å for O(21), O(31), O(23) and O(23'), respectively. The V atom displaced towards the apex of the square pyramid O(11) is distant from this plane by  $0.470(1)$  Å. The short oxygen distance, 2.386 (4) Å, occurs between O(21)O(23) or O(21)O(23'), *i.e.* when  $VO_5$  pyramids are edge-sharing; the shortening of this interatomic distance by some 0.3 Å shows the importance of the  $V^{3+}-V^{5+}$  repulsion. Such repulsion is also responsible for the fact that square  $VO_5$  pyramids sharing edges always have opposite orientations (Bouloux & Galy, 1973).

The structure of  $V_2O_5$  possesses layers built up of  $VO_5$  square pyramids sharing edges and corners; the  $V-O=2.791(3)$  Å interlayer interaction cannot be

treated as a real bond, the structure being, as a result of our recent investigations, easily intercalated by various molecular compounds or complexes (Savariault, 1985).  $V_2O_5$  differs considerably in this case from the other sample sub-oxides, containing both  $V^{5+}$  and  $V^{4+}$  cations, all exhibiting three-dimensional networks:  $V_3O_7$  (Andersson, Galy & Wilhelmi, 1970; Waltersson, Forslund, Wilhelmi, Andersson & Galy, 1974),  $V_4O_9$  (Wilhelmi & Waltersson, 1970), and  $V_6O_{13}$  (Aebi, 1948; Waltersson, Wilhelmi & Kihlborg, 1971).

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### Structure of the Body-Centered Tetragonal $ErRh_4B_4$

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**Abstract.** One of two known forms,  $M_r=622.1$ , tetragonal,  $I4_1/acd$ ,  $a=7.461(2)$ ,  $c=14.804(2)$  Å,  $V=824.1(6)$  Å<sup>3</sup>,  $Z=8$ ,  $D_x=10.03$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha)=0.7107$  Å,  $\mu(\text{Mo } K\alpha)=35.72$  mm<sup>-1</sup>,  $F(000)=2144$ ,  $T=298$  K,  $R=0.051$ , 613 unique reflexions. Synthesized by induction heating. Isostructural with (RE)Ru<sub>4</sub>B<sub>4</sub> (RE = rare earth). In contrast to the atomic arrangements of the other form,

primitive tetragonal, Rh atom tetrahedra are rotated by  $7^\circ$  around the  $c$  axis and B atom tetrahedra are rotated in the same direction but by a slightly smaller amount ( $5^\circ$ ). The shortest connexion between Rh atoms forms zigzag chains running parallel to the  $a_1$  and  $a_2$  axes.

**Introduction.**  $ErRh_4B_4$ , known as a compound exhibiting both superconducting and ferromagnetic behavior,