

On the Crystal Structure of $\text{Cs}_x\text{V}_3\text{O}_7$ ($x \sim 0.35$), a New Hexagonal Vanadium Bronze Structure Type

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A new hexagonal caesium vanadium bronze, $\text{Cs}_x\text{V}_3\text{O}_7$ ($0.3 < x < 0.4$), has been prepared at 670–870 K. The structure of a subcell with $a = 9.880(1)$, $c = 3.605(1)$ Å, $Z = 2$, $V = 305.0$ Å³ has been determined, in terms of $P6_3/m$ symmetry, for a crystal with the composition $\text{Cs}_{0.35}\text{V}_3\text{O}_7$, and refined to an R_w value of 0.032 for 100 independent reflexions and 13 parameters. A new architectural feature is the manner of the three-dimensional linking of the zigzag strings of edge-sharing VO_5 square pyramids to form tunnels in the c direction. There is only one crystallographic V site in the subcell; the average V–O distance is 1.845 Å, close to, but significantly larger than, the grand mean of 1.824 Å for a V^{5+}O_5 polyhedron (observed in well-refined structures of pentavalent V compounds). The actual a axis length is three times, and the c axis five times, the corresponding subcell dimensions, as indicated by a rather weak $hk4$ layer line. An interpretation is proposed in terms of a partial ordering of the Cs atoms in the tunnels. Preliminary investigations of the physical properties show a semiconductor–semiconductor transition, with activation energies of 0.06 eV below and 0.04 eV above the transition temperature of 200 K, and antiferromagnetic behaviour ($T_N = 200$ K).

Introduction

The first structural studies on vanadium bronzes were concerned with $\text{Na}_{2-x}\text{V}_6\text{O}_{15}$ [or $\beta\text{-Na}_{0.33}\text{V}_2\text{O}_5$ for $x = 1$ (Wadsley, 1955), and $\text{Li}_{1+x}\text{V}_3\text{O}_8$ (Wadsley, 1957)]. These two articles have since been followed by many publications describing the structures and properties of vanadium bronzes containing light alkali or alkaline-earth metals, Cu, Zn, *etc.* The results have been summarized by several authors (see, for example, Hagemuller, 1973). Nevertheless, very little has been published about systems with the heavy alkali metals Rb and Cs (see, however, Fotief & Golofkin, 1972; Volkov, Curat & Fotief, 1974).

Within a research programme conducted by Dr Wilhelmi at this Institute, the systems $\text{Cs}_2\text{O}-\text{V}_2\text{O}_5-\text{VO}_2$ and $\text{Rb}_2\text{O}-\text{V}_2\text{O}_5-\text{VO}_2$ are currently being investigated by different techniques (Waltersson & Forslund, 1977). This paper is a report on studies of a new caesium vanadium bronze, $\text{Cs}_x\text{V}_3\text{O}_7$. A report on the physical properties of this material will be published in a forthcoming paper by one of us (BF).

Experimental

By heating finely ground mixtures of CsVO_3 , V_2O_5 and V_2O_3 (mole ratios 4:9:3, corresponding to $\text{Cs}_{0.14}\text{VO}_{2.36}$) in evacuated silica tubes at 580°C for one month, black prism-like crystals of a new hexagonal compound were formed. Different stoichi-

ometries of this compound were achieved by heating mixtures of CsVO_3 , V_2O_5 and V_2O_3 (with gross compositions in the range $\text{Cs}_{0.14}\text{VO}_{2.36}$ to $\text{Cs}_{0.10}\text{VO}_{2.36}$) in evacuated silica tubes for one month at 400–600°C. The products were judged pure from powder photographs.

With atomic-absorption analysis, the Cs/V ratio was found to be in the range 0.119–0.128. The measurements were performed on selected crystals.

The cell dimensions of the hexagonal compound were obtained from a powder photograph, taken with a Guinier–Hägg camera and indexed with the aid of Weissenberg photographs (see Tables 1 and 2).

Two crystals were used for the present X-ray investigation. The first, chosen for the diffractometer work, revealed some disorder (see below). At a later stage of the investigation (when the disorder phenomenon was apparent) another crystal, which had been annealed for two weeks at 450°C, was used. After a prolonged exposure (Cu $K\alpha$ radiation), a rotation photograph of this crystal showed one additional layer line of weak, but distinct, reflexions. This showed the real c axis length to be five times that of the originally assumed value. The layer lines observed were thus those of the $hk0$ (strong), $hk4$ (weak), $hk5$ (strong) and $hk10$ (strong) reflexions. The indexing of the weak $hk4$ layer gave an a axis length three times larger than the value derived for the subcell. Thus the ($3 \times 3 \times 5$) supercell dimensions are: $a = 29.64$, $c = 18.03$ Å, $\gamma = 120^\circ$, and $V = 13714$ Å³.

Single-crystal intensity data for the subcell were collected on a Siemens automatic diffractometer with

monochromatic Mo $K\alpha$ radiation, the θ - 2θ scan technique and a five-point measuring procedure. The crystal used had the dimensions $0.02 \times 0.02 \times 0.04$ (c) mm, and was mounted along the unique c axis.

The scan range for the lattice points was $\Delta\theta = \pm 0.55^\circ$. Two standard reflexions were measured after every 48th lattice point; these indicated no deterioration of the crystal.

The intensities were collected for 348 independent reflexions with $\theta \leq 30^\circ$. Of these, 100 were judged significant from the criterion $\sigma(I)/I \leq 0.40$, where $\sigma(I) = (I_t + I_b)^{1/2}$ and $I = I_t - I_b$.

Lorentz-polarization and absorption corrections

Table 1. Powder pattern of $Cs_xV_3O_7$

Cu $K\alpha_1$ radiation ($\lambda = 1.54050 \text{ \AA}$), KCl internal standard, $a = 6.2930 \text{ \AA}$.

hkl	d_{obs}	$10^5 \sin^2 \theta_{\text{obs}}$	$10^5 \sin^2 \theta_{\text{calc}}$	I_{obs}
1 0 0	8.58	806	810	<i>s</i>
1 1 0	4.948	2423	2431	<i>m</i>
2 0 0	4.283	3235	3242	<i>vs</i>
1 0 1	3.330	5351	5375	<i>vs</i>
2 1 0	3.235	5668	5673	<i>vs</i>
1 1 1	2.913	6991	6996	<i>s</i>
2 0 1	2.758	7802	7806	<i>w</i>
2 2 0	2.473	9701	9725	<i>m</i>
2 1 1	2.4074	10232	10237	<i>m</i>
3 1 0	2.3744	10524	10535	<i>s</i>
4 0 0	2.1378	12982	12966	<i>vw</i>
2 2 1	2.0385	14278	14289	<i>vw</i>
3 1 1	1.9826	15090	15100	<i>vw</i>
4 1 0	1.8679	17004	17018	<i>s</i>
0 0 2	1.8026	18258	18258	<i>m</i>
1 0 2	1.7643	19060	19068	<i>m</i>
2 0 2	1.6612	21500	21499	<i>w</i>
3 3 0	1.6472	21867	21881	<i>vw</i>
5 0 1	1.5457	24831	24824	<i>w</i>
5 1 0	1.5372	25108	25122	<i>w</i>
3 0 2	1.5234	25565	25551	<i>vw</i>
4 2 1	1.4751	27266	27256	<i>m</i>
3 1 2	1.4355	28793	28793	<i>m</i>
5 1 1	1.4134	29698	29687	<i>m</i>
4 0 2	1.3783	31230	31224	<i>vw</i>
5 2 0	1.3697	31626	31606	<i>vw</i>
4 1 2	1.2965	35295	35276	<i>w</i>
5 2 1	1.2802	36201	36170	<i>w</i>

Table 2. The crystal structure of $Cs_xV_3O_7$

Space group $P6_3/m$ (No. 176); subcell dimensions: $a = 9.880(1)$, $c = 3.605(1) \text{ \AA}$, $\gamma = 120^\circ$; cell content: $2Cs_xV_3O_7$.

Atom (n)	Occupancy	Point set	x	y	z	$B (\text{\AA}^2)$
Cs(1)	18.6%	2(<i>b</i>)	0	0	0	2.80(26)
Cs(2)	16.2	2(<i>a</i>)	0	0	$\frac{1}{4}$	2.50(33)
V		6(<i>h</i>)	0.12185 (34)	-0.38144 (30)	$\frac{1}{4}$	0.76(5)
O(1)		6(<i>h</i>)	0.0963 (13)	-0.4516 (11)	$\frac{3}{4}$	1.23(22)
O(2)		6(<i>h</i>)	0.2162 (14)	0.3511 (15)	$\frac{1}{4}$	2.19(25)
O(3)		2(<i>c</i>)	$\frac{1}{3}$	$\frac{2}{3}$	$\frac{1}{4}$	0.43(31)

were applied to the data. The linear absorption coefficient $\mu(\text{Mo } K\alpha) = 71.2 \text{ cm}^{-1}$, calculated for the assumed composition $Cs_{0.4}V_3O_7$, was used in estimating a transmission factor for each reflexion (*International Tables for X-ray Crystallography*, 1962).

Structure determination of the subcell

The structure determination of the subcell was actually performed *before* the $(3 \times 3 \times 5)$ cell was noticed and investigated (see above). Therefore the structure determination and discussion in this section are limited to the subcell and diffractometer data.

The reflexions $00l$: $l = 2n + 1$ were systematically absent, which indicates space groups $P6_3/m$ (No. 176) or $P6_3$ (No. 173).

From a three-dimensional Patterson synthesis, tentative coordinates of the V atoms were derived in point set 6(*h*) of the space group $P6_3/m$. In a following three-dimensional difference Fourier map, three O positions were located, *viz.* two in point set 6(*h*) and one in 2(*c*). The positions were refined with a full-matrix least-squares program to an R_w value of 0.14.

A difference Fourier synthesis was computed with the refined V and O coordinates. The result showed a high density of electrons distributed along the line $x = y = 0$, with the minimum density about 80% of the maximum value. Nonetheless, two maxima were situated at $z = 0$ and $z = \frac{1}{4}$. Therefore Cs atoms were placed in these positions [*i.e.* the point sets 2(*b*) and 2(*a*)].

A least-squares refinement, including Cs occupancy factors and fitting an assumed composition of $Cs_{0.4}V_3O_7$, gave an R_w value of 0.06. The occupancy factors were refined at a late stage of the procedure, leading to a composition of $Cs_{0.35}V_3O_7$. The R_w and R values in the final cycle of refinement were 0.032 and 0.047 respectively, for 100 observations and 13 variables.

The small number of observations is a result of the small dimensions of the single crystal used. The number of zero measurements was 85. When the limit $\sigma(I)/I$ was increased to $\sigma(I)/I \leq 1.0$, the number of accepted observations increased to 177, and R_w and R were

0.041 and 0.084 respectively.* The positional and thermal parameters were the same within the standard deviations, and the e.s.d. values did not change.

In a final ($F_o - F_c$) synthesis the maximum residual peak was situated between the two Cs positions, and was 14% of the smallest O peak in the corresponding F_o synthesis.

Attempts to refine the subcell in space group $P6_3$ were also made. These gave shifts in the z coordinates of the V and O atoms less than 1σ , and about 3σ for the Cs coordinates. Therefore it was assumed that the symmetry of the subcell is $P6_3/m$.

Description of the structure and discussion

Fig. 1 is a projection along the c axis of the subcell and shows zigzag strings built up of square VO_5 pyramids joined by edges, and running in the c direction. This

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32106 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

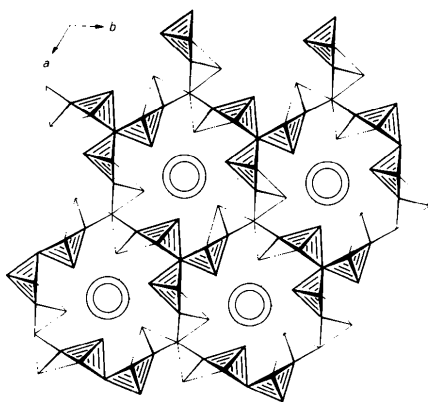


Fig. 1. The structure of the subcell projected on (001).



Fig. 2. The zigzag string of VO_5 square pyramids. The thermal ellipsoids are drawn at 90% probability.

structural element is shown in Fig. 2. Six zigzag strings are linked to each other by corner-sharing to form wide hexagonal tunnels. This method of linking seems to be new, but has also recently been observed in the hexagonal bronze $Cs_xV_2O_5$ (Waltersson & Forslund, 1977). Another way of describing the structure is in terms of two-dimensional sheets formed by zigzag strings sharing corners. Three sets of parallel sheets, hexagonally interpenetrating, form the wide tunnels mentioned above. It is interesting to note that the same kind of stacked two-dimensional sheets is present in the layer structures of $\gamma\text{-Li}_xV_2O_5$ and $\gamma'\text{-Li}_xV_2O_5$ (Galy, 1966). The zigzag strings of VO_5 pyramids are a characteristic structural element found in numerous tetravalent and pentavalent vanadium-oxygen compounds, including minerals with an O:V ratio between 2.2 (approx.) and 3.0 (Evans & Block, 1966) and several vanadium bronzes of light alkali metals (*cf.* Hagemuller, 1973).

Table 3 summarizes the most important interatomic distances and angles observed in the structure.

The mean $^{15}V-O$ distance of 1.845 Å observed in this investigation is slightly, but significantly, larger than the grand mean derived from well-refined pentavalent vanadate structures with the V atoms in five coordination [*viz.* 1.828 (5) Å]. The expected expansion of the polyhedron is associated with the partial reduction of some of the vanadium(V) atoms corresponding to the number of Cs^+ ions in the tunnels.

The different functions of the O atoms can be summarized in the following way. The O(3) atom is the common corner of three square pyramids with the V-O separation 3×1.898 (3) Å. O(1) belongs to three different polyhedra, the V-O distances being $2 \times$

Table 3. Interatomic distances (Å) and bond angles ($^\circ$) in $Cs_xV_4O_7$

E.s.d.'s in the last decimal place are given within parentheses.

Vanadium-oxygen distances			
V-O(2)	1.572 (9)	V-O(1) (2x)	1.902 (3)
-O(3)	1.898 (3)	-O(1)	1.953 (11)
		Bond angles	Oxygen-oxygen distances
O(1)-V-O(1)		142.7 (6)	3.605 (1)
-O(1) (2x)		78.6 (4)	2.443 (15)
-O(2) (2x)		107.8 (3)	2.814 (10)
-O(3) (2x)		91.1 (4)	2.714 (8)
-O(2)		111.1 (5)	2.915 (13)
-O(3)		145.5 (3)	3.678 (11)
O(2)-V-O(3)		103.4 (4)	2.731 (10)
Caesium-oxygen distances			
Cs(2)-O(2) (3x)	3.032 (9)	Cs(2)-O(2) (6x)	3.528 (8)
Cs(1)-O(2) (6x)	3.163 (9)		

1.902(3) and 1.953(11) Å respectively. The O(2) atom has only one V neighbour; the V–O(2) distance of 1.572(9) Å is the shortest (and strongest V–O bond) in the structure. The O(2) atoms form the environment of the Cs atoms in the tunnels.

It is interesting to compare the V–O distances in the zigzag chain with those found in $Cs_{0.3}V_2O_5$ (Waltersson & Forslund, 1977) and γ - $Li_xV_2O_5$ ($0.88 \leq x \leq 1$, the structure reported for $x = 1$ by Galy, Darriet & Hagenmuller, 1971). In these two structures there are two crystallographically different V sites within the zigzag strings. The different formal oxidation numbers of the V atoms in the structures of $Cs_{0.3}V_2O_5$, γ - LiV_2O_5 and $Cs_{0.35}V_3O_7$ are reflected in the V–O distances, as summarized in Table 4.

The V(1) and V(2) atoms in γ - LiV_2O_5 have the valences +4 and +5 respectively (Galy *et al.*, 1971). The formal oxidation numbers are +4.85 and +4.55 in $Cs_{0.3}V_2O_5$ and $Cs_{0.35}V_3O_7$ respectively.

In this context it must be emphasized that the V–O bond distances for $Cs_{0.3}V_2O_5$ and $Cs_{0.35}V_3O_7$ refer to subcell structure determinations (see below).

The shortest V–O distance [V–O(2)] observed in $Cs_{0.35}V_3O_7$ is 1.572 Å. The function of the O(2) atom is exactly the same as that of the O with the shortest V–O distance of 1.570 Å in $Cs_{0.3}V_2O_5$. Both O atoms point into the wide tunnels (see above).

A possible superstructure arrangement

Referring to the $(3 \times 3 \times 5)$ cell, the following reflexions were present: in the $h'k'0$ and $h'k'5$ photographs: $h' = 3n$ and $k' = 3n$, and in the $h'k'4$ photograph: $h' - k' = 3n$ for $h' \neq 3n$ and $k' \neq 3n$.

In an attempt to investigate the superstructure more closely, we made a visual estimation of the 27 independent $h'k'4$ reflexions. After corrections for Lorentz and polarization effects, the $|F_o|$ values (on an arbitrary scale) were calculated.

Starting from the assumptions (a)–(c) below, structure factors were then calculated to match the observed data for all possible $h'k'4$ reflexions.

(a) The superstructure is only due to an ordering of the Cs atoms in the tunnels.

(b) The contributions to $|F_c|$, for the reflexions

$h'k'1-3$ and $h'k'6-9$, are zero (or very low) in accordance with the observations made on the rotation photograph.

(c) The Cs–Cs distance is 4.5 Å, suggested by the observed superstructure interplanar distance.

Several distribution models were tried. One was eventually found which yielded a conventional R of $\sim 10\%$, and gave $|F_c| = 0$ for all the reflexions in (b), except for the $h'k'8$ layer for which $|F_c|$ values were very low. Also, the extinction conditions in the $h'k'4$ layer were fulfilled.

A schematic drawing of the model is shown in Fig. 3. Two sets of Cs atoms were assumed to be present, both with full occupancy within the tunnels and with the

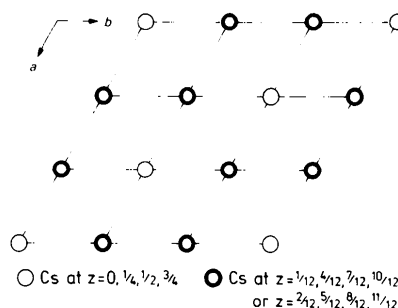


Fig. 3. The model of Cs distribution in the supercell.

Table 5. *The model of Cs distribution in the supercell* ($a = 29.64, c = 18.03$ Å, $\gamma = 120^\circ$)

The first set of Cs atoms

x	y	z
0	0	0, $\frac{1}{4}$, $\frac{1}{2}$ and $\frac{3}{4}$
$\frac{1}{3}$	$\frac{2}{3}$	
$\frac{2}{3}$	$\frac{1}{3}$	
$\frac{1}{3}$	$\frac{1}{3}$	

The second set of Cs atoms

x	y	z
$\frac{1}{12}$	0	$\frac{1}{12}, \frac{4}{12}, \frac{7}{12}$ and $\frac{10}{12}$ or $\frac{2}{12}, \frac{5}{12}, \frac{8}{12}$ and $\frac{11}{12}$
$\frac{4}{12}$	0	
$\frac{7}{12}$	$\frac{1}{12}$	
0	$\frac{1}{12}$	
$\frac{1}{12}$	$\frac{4}{12}$	
0	$\frac{4}{12}$	
$\frac{1}{12}$	$\frac{7}{12}$	
$\frac{4}{12}$	$\frac{7}{12}$	

Table 4. V–O distances (Å) in $Cs_{0.3}V_2O_5$, γ - LiV_2O_5 and $Cs_{0.35}V_3O_7$

	γ - LiV_2O_5		$Cs_{0.3}V_2O_5$		$Cs_{0.35}V_3O_7$
	V(1)	V(2)	V(1)	V(2)	
Apical V–O	1.59	1.61	1.570	1.593	1.572
V–O bond range in pyramid base	1.91–2.00	1.77–1.97	1.80–1.99	1.80–1.97	1.90–1.95
Average of V–O bonds in pyramid base	1.95	1.88	1.894	1.890	1.914

Cs—Cs distance of 4.50 Å. One set was presumed to be completely ordered, while for the other there were two possible distributions in crystallographically equivalent tunnels. No attempt to refine the positional and thermal parameters was made. The parameters of the model are given in Table 5.

With full occupancy of these positions by the Cs atoms, and with the minimum Cs—Cs distance being 4.50 Å, the supercell content is 36 Cs, 270 V and 630 O, giving a composition of $\text{Cs}_2\text{V}_{15}\text{O}_{35}$ or $\text{Cs}_{0.40}\text{V}_3\text{O}_7$. The maximum value of x in the formula $\text{Cs}_x\text{V}_3\text{O}_7$ is accordingly 0.40.

In the structural studies of $\text{Cs}_{0.3}\text{V}_2\text{O}_5$ (Waltersson & Forslund, 1977), the presence of a supercell has also been observed; it is assumed to arise from an ordering of the Cs atoms in the tunnels (see above). The observed interplanar distance is 5.1 Å, the probable Cs—Cs separation within the tunnels.

Physical properties

Measurements of the magnetic susceptibility by the Faraday method on polycrystalline samples in the temperature range 78–700 K revealed antiferromagnetic behaviour of $\text{Cs}_x\text{V}_3\text{O}_7$, with a Néel point close to 200 K.

Measurements of the electrical conductivity on a single crystal in the range 90–400 K showed the compound to be a semiconductor with a transition at about

200 K, and activation energies of 0.04 eV above this temperature and 0.06 eV below.

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