

The Crystal Structure of VOMoO_4

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The compound VMoO_5 has been found to be isostructural with MoOPO_4 and, accordingly, should be formulated as VOMoO_4 . The tetragonal unit cell ($a = 6.6078 \pm 0.0002 \text{ \AA}$, $c = 4.2646 \pm 0.0003 \text{ \AA}$) contains two formula units of VOMoO_4 in the space group $P4/n$. Atomic parameters were refined by the method of least squares.

The structure consists of VO_6 octahedra joined by apices to form chains which run parallel to the c axis. Each octahedron is also connected to four MoO_4 tetrahedra by corner sharing, thereby producing a three-dimensional network. Alternatively, the structure can be described as a slightly distorted cubic close-packed arrangement of oxygen atoms in which some of the octahedral holes are occupied by vanadium atoms and some of the tetrahedral holes by molybdenum atoms. The MoO_4 tetrahedra are regular within experimental error; the VO_6 octahedra are distorted considerably and might be considered square pyramids. The structure is discussed and compared with other related phases.

The narrow homogeneity range exhibited by this phase is discussed from a structural point of view.

During the course of a detailed study of the ternary Mo-V-O system, a phase of the composition VMoO_5 was observed.¹ Cell dimensions and space group symmetry obtained from the powder diffraction pattern indicated that the structure of this compound might be the same as that recently reported for MoOPO_4 .² Preliminary calculations of structure factors for different structure models indicated that molybdenum probably occupied the tetrahedral positions in the MoOPO_4 structure, while vanadium occupied the octahedral sites. To verify this supposition and to determine accurate interatomic parameters, a structure analysis was undertaken. A brief report of the results of this study has appeared elsewhere.³

A phase of the same composition has been reported recently by Tridot *et al.*,⁴ who list d -values and relative intensities. Their values agree with those reported in this work, but they list no structural details.

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Table 1. X-Ray powder diffraction data for VOMoO₄, CuKα₁ radiation (λ = 1.54051 Å).

<i>I</i>	<i>d</i> _{obs}	sin ² θ _{obs} × 10 ⁵	<i>hkl</i>	(sin ² θ _{obs} - sin ² θ _{calc}) × 10 ⁵
w+	4.674 Å	2 716	110	- 2
w	4.264	3 263	001	+ 1
m	3.581	4 628	101	+ 7
s	3.303	5 438	200	+ 3
vs	3.147	5 992	111	+ 12
w+	2.613	8 699	201	+ 2
vw	2.429	10 055	211	- 1
w+	2.337	10 867	220	- 4
vw	2.090	13 578	310	- 10
w	2.049	14 127	221	- 6
vw	2.029	14 412	102	+ 4
w+	1.957	15 488	301	- 4
m	1.939	15 774	112	+ 7
vs	1.876	16 856	311	- 6
w	1.792	18 479	202	- 5
w-	1.770	19 839	212	- 4
vw	1.684	20 923	321	- 4
m	1.652	21 733	400	- 8
w+	1.575	23 918	222	- 2
w	1.557	24 465	330	+ 7
vw-	1.533	25 255	302	- 24
w-	1.500	26 362	411	0
s	1.493	26 627	312	- 10
m	1.478	27 165	420	- 11
w+	1.463	27 713	331	- 8
vw	1.421	29 375	003	+ 15
w	1.396	30 429	421	- 10
vw	1.390	30 718	{322	+ 4
vw	1.360	32 083	{103	- 1
m	1.305	34 811	113	+ 5
w-	1.296	35 325	{402	+ 21
vw	1.281	36 147	{203	+ 15
vw	1.263	37 227	510	- 4
w+	1.258	37 511	{412	- 2
m	1.240	38 599	{213	- 7
m	1.214	40 251	{501	- 6
w-	1.176	42 941	{431	- 6
w+	1.168	43 487	332	+ 3
w-	1.133	46 207	511	+ 8
w-	1.127	46 769	{422	+ 26
w-	1.223	47 044	{223	+ 20
m	1.107	48 376	313	- 8
w	1.101	48 920	440	+ 5
m+	1.095	49 458	530	+ 7
			441	+ 25
			{502	+ 25
			{432	+ 25
			{323	+ 19
			512	- 2
			600	+ 3
			531	- 4

EXPERIMENTAL

Single crystals were prepared by sealing mixtures of V_2O_5 , V_2O_3 , and MoO_3 in the atom ratio V:Mo:O of 1:1:5, into thin-walled 3 mm diameter evacuated platinum tubes, which were subsequently sealed into evacuated silica. The ampoules were heated at 900°C for times varying from three to five days. The product consisted of almost black crystals which were transparent in thin sections, exhibiting a reddish brown tinge.

Lattice parameters of the tetragonal unit cell were calculated from an X-ray powder diffraction photograph taken with monochromatized $CuK\alpha_1$ radiation in a Guinier-type focusing camera. With potassium chloride ($a = 6.29228 \text{ \AA}$ at 25°C)⁶ as an internal standard, the $\sin^2\theta$ values listed in Table 1 were calculated. The unit cell dimensions, together with their standard deviations, obtained by a least squares refinement procedure (Program No. 6018)⁶ and the unit cell volume are given in Table 2.

The observed density of the powder, determined from the apparent loss of weight in chloroform, was $4.02 \pm 0.02 \text{ g/cm}^3$. A value of 4.06 g/cm^3 is calculated on the basis of two formula units of $VMoO_5$ per unit cell.

A somewhat irregularly-shaped rectangular platelet, 0.032 mm (a) \times 0.042 mm (b) \times 0.013 mm (c) was mounted and rotated around the a -axis. Integrated Weissenberg photographs were taken by the multiple film technique with $CuK\alpha$ radiation. Relative intensities of the seven layer lines, $0kl-6kl$, were measured photometrically. The data were corrected for absorption (Program No. 6019)^{6,7} by using a linear absorption coefficient, $\mu = 507 \text{ cm}^{-1}$, derived from atomic absorption coefficients compiled in the *International Tables*.⁸ All computational work was carried out on the electronic computer FACIT EDB, using, in addition to the programs described previously, programs for the Lorentz-polarization correction (No. 6024), least squares refinement (No. 6023), calculation of interatomic distances and angles (No. 6016), and calculation of standard deviations of interatomic distances. The last program, designated STINTA, has been written recently by Dr. R. Norrestam of this institute. The least squares program is based on the block diagonal matrix approximation including individual, isotropic temperature factors. Atomic scattering factor curves for unionized atoms as given for vanadium and molybdenum by Thomas and Umeda,⁹ and for oxygen by Freeman,¹⁰ were used in these calculations. The real part of the dispersion correction¹¹ was applied to the scattering factor curves.

STRUCTURE REFINEMENT

The coordinates determined for the $MoOPO_4$ structure,² modified slightly to account for the expected size difference between the PO_4 and the MoO_4 tetrahedra, were used as starting parameters. Using a total of 306 independently

Table 2. The crystal structure of $VOMoO_4$.

Space group: $P4/n$ (No. 85).

Unit cell dimensions: $a = 6.6078 \pm 0.0002 \text{ \AA}$

$c = 4.2646 \pm 0.0003 \text{ \AA}$, $V = 186.2 \text{ \AA}^3$.

Cell content: 2 $VOMoO_4$.

2 V and 2 O_1 in $2 \times 2(c)$: $(\frac{1}{2}, \frac{1}{2}, z; \frac{3}{2}, \frac{3}{2}, \bar{z})$

2 Mo in $2(b)$: $(\frac{1}{2}, \frac{3}{2}, \frac{1}{2}; \frac{3}{2}, \frac{1}{2}, \frac{1}{2})$

8 O_2 in $8(g)$: $(x, y, z; \frac{1}{2} - x, \frac{1}{2} - y, z; \frac{1}{2} - y, x, z; y, \frac{1}{2} - x, z; \bar{x}, \bar{y}, z; \frac{1}{2} + x, \frac{1}{2} + y, \bar{z}; \frac{1}{2} + y, \bar{x}, \bar{z}; \bar{y}, \frac{1}{2} + x, \bar{z})$

Atom	$x \pm \sigma(x)$	$y \pm \sigma(y)$	$z \pm \sigma(z)$	$B \pm \sigma(B)$
V	$\frac{1}{2}$	$\frac{1}{2}$	0.8395 ± 0.0007	0.354 ± 0.040
Mo	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{1}{2}$	0.376 ± 0.018
O_1	$\frac{1}{2}$	$\frac{1}{2}$	0.2327 ± 0.0037	2.58 ± 0.32
O_2	0.7034 ± 0.0019	0.4623 ± 0.0019	0.2597 ± 0.0019	1.06 ± 0.17

Table 3. Weight analysis obtained in the final cycle of the least squares refinement of VOMoO₄.

Interval $\sin \theta$	No. of reflections	$\overline{w \Delta^2}$	Interval F_{obs}	No. of reflections	$\overline{w \Delta^2}$
0.00—0.46	44	1.30	0—8	0	
0.46—0.58	33	0.80	8—16	38	1.16
0.58—0.67	39	0.86	16—24	78	1.08
0.67—0.74	36	1.06	24—32	42	1.05
0.74—0.79	30	1.25	32—40	43	0.61
0.79—0.84	28	1.79	40—48	36	0.95
0.84—0.89	29	0.51	48—56	24	1.61
0.89—0.93	27	0.72	56—64	18	0.50
0.93—0.97	30	0.83	64—72	15	1.26
0.97—1.00	9	0.32	> 72	11	0.56

measured reflections covering a quadrant of the reciprocal space, these coordinates were refined by the least squares program until the shifts in the parameters were less than 10 % of their standard deviations. Only the strongest reflection was considered to suffer seriously from extinction and was deleted during the process of refinement. When the refinement was stopped, the discrepancy index, R , defined in the usual way and including observed reflections only, equalled 0.053.

Because of restrictions in the least squares program, the structure had to be described and refined in orthorhombic or lower symmetry. The point position 8(g) of space group $P4/n$, which is occupied by oxygen atoms O₂ (cf. Table 2), was split into two four-fold positions ($x, y, z; \frac{1}{2}-x, \frac{1}{2}-y, z; \bar{x}, \bar{y}, \bar{z}; \frac{1}{2}+x, \frac{1}{2}+y, \bar{z}$). These correspond to the general positions 4(g) of the space group $P2/b$ which is a sub-group of $P4/n$. However, within the limits of the standard deviations, no significant departure from tetragonal symmetry was observed in the final calculations, and the description of the structure in the space group $P4/n$ seems justifiable.

Cruckshank's weighting function $w = 1/(A + |F_o| + C |F_o|^2)$, was used in the refinement. The value used for the constant A was 34 and that for C was 0.02. The weight analysis obtained in the last cycle is presented in Table 3. In this table, w is the weighting factor and $\Delta = (|F_o - \bar{F}_c|)$.

The atomic parameters obtained in the last cycle of the refinement are listed in Table 2. The parameters given for oxygen atom O₂ are the average of the two parameters determined in the last least squares cycle for the four-fold positions. The standard deviations reported were determined from the standard deviations obtained for the four-fold positions by the usual statistical methods.

Observed and calculated structure factors have been listed in a separate document¹² which may be obtained from the secretary of this institute.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure consists of distorted VO_6 octahedra, linked together at their apices (oxygen O_1) to form chains which run parallel to the c axis. These chains are connected by MoO_4 tetrahedra so that each octahedron shares corners with four molybdate tetrahedra. Since each corner of the tetrahedra is joined to a different octahedron, a three-dimensional network results. The structure described in this manner is illustrated in Fig. 1.

Alternatively, the structure may be described in terms of a slightly distorted cubic close-packed arrangement of oxygen atoms in which 1/5 of the octahedral holes are occupied by vanadium atoms (molybdenum atoms in MoOPO_4) and 1/10 of the tetrahedral holes by molybdenum atoms (phosphorus atoms in MoOPO_4). The idealized close-packed structure is shown in Fig. 2.

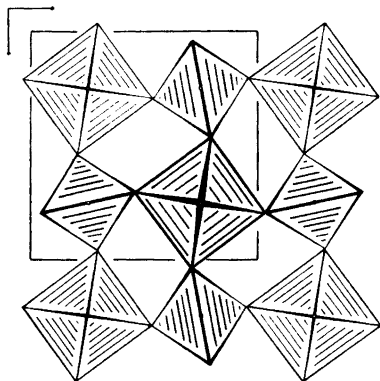


Fig. 1. The structure of VOMoO_4 viewed along $[001]$. Strings of VO_6 octahedra (at two levels) run parallel to the line of sight and are connected by MoO_4 tetrahedra.

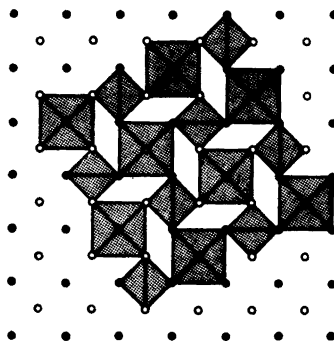


Fig. 2. The ideal structure of VOMoO_4 obtained by filling metal atoms into octahedral and tetrahedral interstices (shaded) of a face-centered cubic oxygen lattice.

The axial ratio, c/a , is 0.646 in the present compound and 0.696 in MoOPO_4 , compared with the theoretical value of 0.632 for an undistorted close-packed arrangement. Although these values seem to indicate that VOMoO_4 is the more ideal of the two structures, the oxygen volume, V_{O} , shows that MoOPO_4 has in fact a more dense oxygen packing. The value, V_{O} , derived by dividing the unit cell volume by the number of oxygen atoms in the cell, is 18.6 \AA^3 in VOMoO_4 and 16.4 \AA^3 in MoOPO_4 . The theoretical value for ideal closest packing of spheres with the radius 1.40 \AA is 15.5 \AA^3 . An analysis of bond distances in the two structures indicates that this difference in oxygen packing is due almost entirely to the difference in size between the MoO_4 and PO_4 groups.

The crystal structure of an analogous compound, VOSO_4 , has recently been determined by Kierkegaard and Longo.¹³ This compound is not isostructural with the two discussed above, even though it is built up of similar chains of VO_6 octahedra which are connected by tetrahedra. Its oxygen volume, V_{O} , is as low as that observed in MoOPO_4 .

Table 4. Interatomic distances and selected bond angles together with their standard deviations in VOMoO₄.

<i>Within octahedra:</i>			
V—O ₁	O ₁ —V		1.677 ± 0.016 Å
V—O ₁	O ₁ —V		2.588 ± 0.016
V—4O ₂		O ₂ —V (4×)	1.972 ± 0.013
	O ₁ —4O ₂	O ₂ —O ₁ (4×)	2.897 ± 0.016
	O ₁ —4O ₂	O ₂ —O ₁ (4×)	2.849 ± 0.016
		O ₂ —2O ₂ (2×)	2.723 ± 0.018
<i>Within tetrahedra:</i>			
Mo—4O ₂		O ₂ —Mo (4×)	1.764 ± 0.012
		O ₂ —2O ₂ (2×)	2.885 ± 0.018
		O ₂ —O ₂ (2×)	2.872 ± 0.015
<i>Between neighboring polyhedra:</i>			
	O ₁ —4O ₂	O ₂ —O ₁	3.306 ± 0.018
		O ₂ —O ₂	3.39 ± 0.02
		O ₂ —O ₂	3.53 ± 0.02
		O ₂ —2O ₂	3.003 ± 0.015
<i>Bond angles:</i>			
O ₁ —V—O ₂		102.4 ± 0.6°	
O ₂ —V—O ₂		87.3 ± 0.8	
O ₂ —V—O ₂		155.2 ± 1.0	
O ₂ —Mo—O ₂		109.5 ± 0.8	

Interatomic distances and selected bond angles determined for the VOMoO₄ structure are presented in Table 4. These data indicate that although the vanadium atoms are situated within fairly regular oxygen octahedra, they are subjected to a considerable off-center distortion such that one of the V—O bonds has become rather short and the opposite one long. This distortion differs only slightly from the Mo coordination in MoOPO₄ and compares favorably with the V(IV) coordination in duttonite, VO(OH)₂ (V—O 1.65, 2.02 (4×), 2.30 Å).¹⁴ The same type of distortion exists in VOSO₄, but the extremely short and long V—O distances are smaller by 0.083 and 0.304 Å, respectively, in that structure, while the remaining four (equatorial) bonds are 0.033–0.084 Å longer. In VO₂,¹⁵ the octahedra are less distorted — the V—O bond distances range from 1.763 to 2.064 Å.¹⁶ However, other features of this structure, for instance, the occurrence of direct V—V bonds, make a comparison less meaningful.

The MoO₄ tetrahedra are regular within the experimental error. The Mo—O distances agree well with the value 1.772 ± 0.006 Å reported for PbMoO₄,¹⁷ and 1.71–1.79 Å (mean value 1.76 Å) obtained by a recent refinement¹⁸ for the tetrahedral Mo—O bonds in Na₂Mo₂O₇.

From the structural analogy with the isomorphous or structurally related compounds MoOPO₄, NbOPO₄ (isomorphous with MoOPO₄),¹⁹ and VOSO₄, the formula VOMoO₄ seems appropriate. The fact that the crystals are not completely opaque supports the assumption that the metal atoms are in fixed valence states. The similarity of the coordination around the metal atoms

in the present phase and the compounds indicated above which contain V(IV) and Mo(VI) substantiates further its formulation as a vanadium(IV) oxide molybdate(VI).

STOICHIOMETRY

A single phase has been prepared only at the composition VMoO_5 . The cell dimensions given in Table 2 refer to a specimen of this composition. However, slightly different lattice parameters have been observed in two- or three-phase mixtures of other gross compositions. These variations seem to depend mainly on the V/Mo ratio and may indicate a narrow homogeneity range, $(\text{V}_x\text{Mo}_{2-x})\text{O}_5$, where x probably may differ from 1 by a maximum of only a few hundredths. The following cell dimensions indicate the deviations in the lattice parameters. (The errors indicated are standard deviations in the last decimal place.)

Composition:	Mo-rich	Stoichiometric	V-rich
a	6.6091 (± 6)	6.6078 (± 2)	6.5922 (± 4) Å
c	4.2612 (± 9)	4.2646 (± 3)	4.2665 (± 7) Å

From a structural viewpoint, vanadium atoms can probably replace molybdenum atoms and *vice versa*. The observed variations in the cell dimensions can be explained qualitatively by such a mechanism. However, in this paper arguments will be presented only for the case where the effect is greatest; *viz.*, the vanadium rich side.

In the V-rich oxide specimens, some V atoms must have replaced Mo atoms in the tetrahedra — interstitial V atoms or Mo vacancies seem improbable. Pentavalent vanadium in tetrahedral coordination is well known, for example, in KVO_3 and NH_4VO_3 where the mean V—O distance is 1.73 Å.¹⁴ Almost the same mean value, 1.74 Å, is obtained from the values for tetrahedrally coordinated ortho- and polyvanadates listed in the *International Tables*.⁸ Thus, a VO_4 tetrahedron may be considered slightly smaller than a MoO_4 tetrahedron, and the substitution should accordingly bring the strings of octahedra closer together and cause the a axis to decrease (*cf.* MoOPO_4). The substitution of V(V) for Mo(VI) implies a simultaneous oxidation of some of the octahedral vanadium from V(IV) to V(V) or, alternatively, and in our opinion less probable, the introduction of oxygen vacancies. A comparison with the "octahedral" coordination in V(V) compounds; for instance, V_2O_5 ,^{20,21} indicates that increasing the valence state of vanadium should simultaneously cause the four equatorial V—O bonds to be shortened (thereby enhancing the shortening of the a axis) and the axial bonds of the octahedron to lengthen. These conclusions are in agreement with the observed slight increase in the length of the c axis.

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