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The Crystal Structure of $(Mo_{0.3}V_{0.7})_2O_5$ of R-Nb_2O_5 type and a Comparison with the Structures of V_2O_5 and V_2MoO_8

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$(Mo_{0.3}V_{0.7})_2O_5$ represents the molybdenum rich limit (at 650°C) of a range of solid solution extending from V_2O_5 along the line $(Mo_xV_{1-x})_2O_5$ in the Mo—V—O system. There are, however, discontinuities within this range associated with symmetry changes. This phase has been studied by single crystal diffraction methods. The dimensions of the monoclinic unit cell are a = 11.809 Å, b = 3.652 Å, c = 4.174 Å, β = 90.56°, and the space group is $C2$.

The structure is of the same type as that of R-Nb_2O_5 and can be considered as composed of MO_6 octahedra coupled in the same way as in V_2O_5, although the distortion of the metal atoms within the octahedra follows a different pattern. This distortion, as reflected in the considerable divergence of the M—O bond lengths, is intermediate in magnitude between that in V_2O_5 and MoO_3. Molybdenum and vanadium atoms are randomly distributed over the metal atom positions.

The structure is also closely related to that of V_2MoO_8.

In the course of an investigation of the phases formed in the system V—Mo—O [1] it has been observed that molybdenum may replace vanadium in V_2O_5. This replacement gives rise to a range of solid solution, $(Mo_xV_{1-x})_2O_5$, extending at 650°C to the composition $(Mo_{0.3}V_{0.7})_2O_5$ approximately. To a first approximation the unit cell dimensions vary gradually within this interval but a closer examination of the powder patterns and comparison with single crystal photographs revealed that the symmetry has changed from orthorhombic for V_2O_5 to monoclinic for $(Mo_{0.3}V_{0.7})_2O_5$. According to preliminary results, this transition occurs at a composition of about $x = 0.20$ and is probably associated with the occurrence at this composition of a phase giving a more complex powder pattern. Further studies of these problems are in progress.

This article presents a structure determination of a crystal with a composition close to the molybdenum-rich limit. A short communication of the investigations reported below was given at the Seventh International Congress of Crystallography.[2]

EXPERIMENTAL

The crystal studied was selected from a sample prepared by heating a mixture of MoO_3, V_2O_5, and V_2O_3 of gross composition $Mo_{0.3}V_{0.7}O_{2.5}$ in a sealed silica tube at 650°C for 2 days. The powder pattern of this sample showed the lines (Table 1) of a phase which could be indexed on the basis of a monoclinic unit cell with the dimensions given in Table 2. A few additional weak lines could be assigned to $VOMoO_4$[3] and it seems therefore probable that the monoclinic phase contained slightly less molybdenum than indicated by the gross composition and that its formula should be approximately $(Mo_{0.28}V_{0.72})_2O_5$.

The crystal was shaped like a somewhat truncated parallelepiped with the dimensions 0.0204 mm (along a), 0.0636 mm (along b), and 0.0053 mm (along c). Integrated Weissenberg photographs were recorded of the $h0l$, $h1l$ and $h2l$ layer lines using Cu$K\alpha$ radiation and multiple film technique. The relative intensities of the reflections were measured by

Table 1. X-Ray powder diffraction data for $(Mo_{0.3}V_{0.7})_2O_5$, Cu$K\alpha_1$ radiation (λ = 1.54051 Å).

I	d_{obs} Å	$\sin^2\theta_{obs} \times 10^5$	hkl	$(\sin^2\theta_{obs} - \sin^2\theta_{calc}) \times 10^5$
w	5.894	1708	200	+ 6
w+	4.169	3414	001	+ 9
st	3.487	4878	110	+ 5
w	3.419	5074	$\bar{2}01$	+14
w	3.392	5157	201	+ 2
w+	2.952	6810	400	+ 3
st	2.678	8270	111	+32
			310	− 7
			$\bar{1}11$	−16
vw	2.420	10131	$\bar{4}01$	+13
vw	2.087	13621	002	0
w	1.9685	15311	600	− 6
vw	1.9638	15384	202	−34
m	1.8270	17775	020	−15
w	1.7980	18353	$\bar{5}11$	−17
w	1.7944	18426	$\bar{1}12$	−20
vw	1.7458	19466	220	−26
vw	1.7117	20250	$\bar{4}02$	+12
w	1.6738	21178	021	−17
w	1.6086	22927	221	−18
w+	1.5533	24589	420	− 9
m	1.5316	25293	710	− 2
vw	1.4583	27898	$\bar{4}21$	−10
w	1.4438	28461	$\bar{5}12$	− 7
vw	1.4415	28551	$\bar{7}11$	+17
m	1.3386	33110	620	+ 3
w	1.2722	36659	621	+ 4
vw	1.2541	37724	403	−15
vw	1.2488	38046	$\bar{4}22$	+17
vw	1.2109	40460	$\bar{8}02$	−11
			130	+ 6
vw	1.1809	42545	911	+17
			10,0,0	− 1
w	1.1633	43841	$\bar{1}31$	+ 6
			330	−16
vw	1.1235	47000	622	−13
vw	1.1214	47175	$\bar{3}31$	−16
vw	1.1197	47325	331	− 9

means of a densitometer. These values were corrected for the effect of absorption (crystal assumed to be bounded by 7 planes; $\mu = 496$ cm^{-1}) and the usual Lp-correction was applied. These calculations as well as the subsequent structure factor calculations, least-squares refinement and calculations of interatomic distances were performed on a computer of type FACIT EDB by means of the programs No. 6015, 6016, 6019, 6023, and 6030 [4] (the Lp-program written by B. Lundberg is not listed in Ref. 4). The atomic scattering factors listed in *International Tables* [5] were used, namely, for neutral oxygen and vanadium the values given in Table 3.3.1 A and for molybdenum those given in Table 3.3.1 B. The real part of the dispersion correction [5] was applied to these values.

DETERMINATION AND REFINEMENT OF THE STRUCTURE

Systematic extinction was observed for all reflections hkl with $h + k = 2n + 1$. Together with the observed Laue symmetry $2/m$ this led to the three possible space groups $C2/m$ (No. 12), $C2$ (No. 5), and Cm (No. 8).

The fact that the crystal under investigation represented one end of a range of solid solution (*cf.* above) the other limit of which is V_2O_5 suggested a close relationship between the crystal structures. The space group of V_2O_5 is $Pmnm$ (No. 59) [6,7] or possibly $Pmn2_1$ (No. 31) [7] which, on the other hand, implies a basic difference between the two structures.

A model was tried in which the arrangement of MO_6 octahedra was the same as in V_2O_5 but in which the distortion of the metal atoms from the centres of these octahedra was different to account for the different symmetry. Structure factor calculations and least squares refinement proved this model to be correct. The structure is shown in Fig. 1 together with that of V_2O_5. Completely random distribution of molybdenum and vanadium atoms over the metal atom positions had to be assumed since these positions were crystallographically equivalent and no indication of a superstructure had been observed on the X-ray photographs. Because of the uncertainty in the exact composition of the crystal (*cf.* above) three different Mo:V ratios were tested, *viz.* M = (0.33 Mo + 0.67 V), (0.30 Mo + 0.70 V), and (0.27 Mo + 0.73 V). The results, obtained by least squares refinement, differed only insignificantly, however.

The space group Cm was hardly consistent with the structure model but the remaining two, $C2/m$ and $C2$, were both possible. Least squares refinement was carried out for both alternatives, namely (I) 1 M and 2 O in positions $4i$, and 1 O in $2a$ of space group $C2/m$ and (II) 1 M and 2 O in $4c$ and 1 O in $2a$ of space group $C2$. The final R-values (based on observed reflections only) were about the same for both alternatives, *viz.* 0.071 and 0.070, respectively, but the final y coordinates of O(1) and O(2) in alternative II differed by 7.0σ and 5.1σ, respectively, (σ = the corresponding standard deviation) from the values 0 and $\frac{1}{2}$ at which they are fixed by symmetry in alternative I. The temperature factors obtained were also less divergent in alt. II than in alt. I and, particularly, they were much lower for atoms O(1) and O(2) in alt. II. It was thus evident that the structure is best described in the non-centrosymmetric space group $C2$ and the final parameters for this case are given in Table 2.

Weights in the least squares procedure were calculated according to Cruickshank's formula, $w = 1/(A + F_o + C \cdot F_o^2)$, where the following values were chosen for the parameters, $A = 18$, $C = 0.012$. The final weight analysis is given in Table 3. The observed and calculated structure factors are listed in Table 4.

Table 2. The crystal structure of $(Mo_{0.3}V_{0.7})_2O_5$.

Space-group: $C2$ (No.5)
Unit cell dimensions:* $a = 11.809$ ($\pm$ 2) Å
$b = 3.652$ ($\pm$ 1) Å
$c = 4.174$ ($\pm$ 1) Å
$\beta = 90.56$ ($\pm$ 2) °

Unit cell content: 2 M_2O_5, $M = (Mo_{0.28}V_{0.72})$, Mo/V ratio approximative (see text).

Atom	Position	$x \pm \sigma(x)$	$y \pm \sigma(y)$	$z \pm \sigma(z)$	$B \pm \sigma(B)$
M	4c	0.14892 $\pm$ 0.00025	0	0.10034 $\pm$ 0.00076	0.441 $\pm$ 0.038
O(1)	4c	0.1446 $\pm$ 0.0015	0.065 $\pm$ 0.0088	0.4934 $\pm$ 0.0042	1.09 $\pm$ 0.32
O(2)	4c	0.1792 $\pm$ 0.0013	0.552 $\pm$ 0.010	0.9953 $\pm$ 0.0037	0.51 $\pm$ 0.26
O(3)	2a	0	0.002 $\pm$ 0.034	0	1.73 $\pm$ 0.47

* a[KCl, 25°C] = 6.29228 Å.[13]

DISCUSSION

The structure of $(Mo_{0.3}V_{0.7})_2O_5$ turns out to be isotypic with that recently suggested by Gruehn for R-Nb_2O_5 on the basis of powder diffraction data.[6] The unit cell dimensions given for R-Nb_2O_5 are (the a and c axes interchanged here), $a = 12.7_9$ Å, $b = 3.82_6$ Å, $c = 3.98_3$ Å, $\beta = 90.7_5$°. The space group was assumed to be ($A2/m =$) $C2/m$ and the following atomic coordinates were reported (the numbering of the atoms changed here to become analogous with that in Table 2).

Table 3. Weight analysis obtained in the last cycle of refinement. $\Delta = ||F_{obs}| - |F_{calc}||$, w = weighting factor. The $\overline{w\Delta^2}$ values have been normalized.

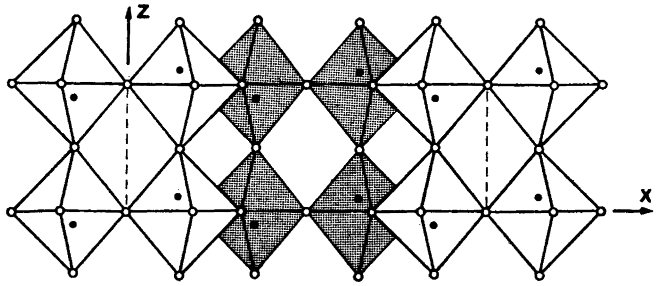
Interval $\sin\theta$	Number of independent reflections	$\overline{w\Delta^2}$	Interval $\|F_{obs}\|$	Number of independent reflections	$\overline{w\Delta^2}$
0.00−0.46	26	0.71	0−16	3	0.47
0.46−0.58	21	0.84	16−24	7	1.75
0.58−0.67	15	1.49	24−32	29	1.19
0.67−0.74	15	0.82	32−40	32	1.11
0.74−0.79	13	0.51	40−48	19	1.04
0.79−0.84	11	1.20	48−56	18	0.60
0.84−0.89	10	0.99	56−64	14	0.86
0.89−0.93	7	1.28	64−72	7	0.76
0.93−0.97	15	0.82	> 72	10	0.73
0.97−1.00	6	2.94			

	x	y	z
Nb	0.146	0	0.07
O(1)	0.16	0	0.5
O(2)	0.18	0.5	0
O(3)	0	0	0

A comparison with Table 2 emphasizes the similarity between the two structures. The discussion below, therefore, applies also to R-Nb_2O_5.

The coordination of oxygen atoms around vanadium in V_2O_5 may be described either as five- or sixfold since the sixth V—O bond is considerably longer than the other five.[7,8] If the coordination is regarded as six-fold the structure may be described as built up of octahedra sharing edges and corners as visualized in Fig. 1 *b*. Comparison with Fig. 1 *a* indicates that the coupling of the octahedra is the same in $(Mo_{0.3}V_{0.7})_2O_5$. The structures can thus be described as built of edge sharing octahedra which form zig-zag chains that run in the *b* direction. These chains are mutually connected by corner sharing between octahedra in adjacent chains. Alternatively, they may be regarded as consisting of slabs of ReO_3-type, two octahedra thick, which extend infinitely in the *bc* plane; these, in turn, are interconnected by edge-sharing between

a



b

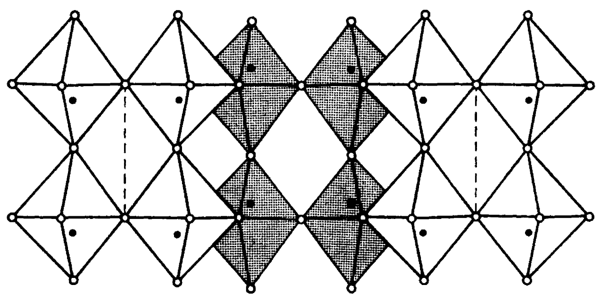


Fig. 1. The structures of (*a*) $(Mo_{0.3}V_{0.7})_2O_5$ and (*b*) V_2O_5 visualized as built up of MO_6 octahedra at two levels (light and shaded, respectively). These polyhedra share corners with crystallographically identical ones above and below. The positions of the metal inside the octahedra are indicated by dots.

Table 4. Observed and calculated structure amplitudes and calculated phase angles (expressed as a fraction of one cycle). $\Delta = ||F_{obs}| - |F_{calc}||$. The values of $\Delta \sqrt{w}$ have been normalized.

h	k	l	$\|F_{obs}\|$	$\|F_{calc}\|$	$\Delta \sqrt{w}$	α
2	0	3	59.3	60.4	0.24	0.00000
-6	0	3	38.5	37.6	0.19	0.50000
-2	0	4	32.8	31.6	0.35	0.00000
-6	0	4	27.6	28.3	0.38	0.50000
-10	0	3	30.4	26.4	1.24	0.00000
-12	0	3	31.0	31.5	0.15	0.50000
-4	0	5	32.9	35.7	0.83	0.00000
-14	0	2	24.9	27.0	0.69	0.00000
-10	0	4	25.6	29.7	1.31	0.00000
0	0	5	34.6	34.8	0.05	0.50000
4	0	5	30.9	34.4	1.08	0.00000
8	0	4	32.7	32.4	0.09	0.50000
4	0	4	37.8	39.0	0.31	0.00000
2	0	3	50.3	48.8	0.38	0.50000
4	0	3	50.3	55.7	1.34	0.00000
8	0	3	54.3	55.3	0.25	0.50000
0	0	2	74.9	70.6	0.89	0.00000
2	0	2	74.2	80.6	1.30	0.50000
6	0	2	71.4	76.7	1.11	0.00000
8	0	2	45.7	41.5	1.10	0.50000
12	0	2	42.2	46.5	1.18	0.00000
12	0	3	34.9	38.1	0.94	0.00000
12	0	1	49.4	41.8	1.91	0.00000
10	0	1	32.2	29.4	0.86	0.50000
8	0	1	32.3	28.7	1.08	0.50000
6	0	1	81.7	83.9	0.43	0.00000
2	0	1	65.5	72.4	1.52	0.50000
0	0	1	88.9	92.5	0.65	0.00000
2	0	0	42.8	41.8	0.27	0.50000
4	0	0	81.4	87.6	1.20	0.50000
6	0	0	93.0	96.0	0.54	0.00000
8	0	0	21.5	23.4	0.64	0.00000
10	0	0	57.1	55.2	0.45	0.50000
14	0	0	38.9	34.0	1.35	0.00000
2	0	-1	37.8	33.0	1.35	0.00000
4	0	-1	57.9	58.2	0.08	0.50000
6	0	-1	34.6	30.2	1.29	0.00000
8	0	-1	45.4	38.7	1.76	0.00000
10	0	-1	28.1	24.5	1.14	0.50000
14	0	-1	31.6	28.2	1.04	0.00000
2	0	-2	56.6	52.3	1.01	0.00000
4	0	-2	64.2	63.0	0.27	0.50000
8	0	-2	59.1	53.2	1.38	0.00000
12	0	-2	32.5	28.9	1.10	0.50000
14	0	-2	23.0	27.0	1.34	0.00000
6	0	-3	41.1	37.6	0.96	0.50000
8	0	-3	30.3	27.8	0.79	0.00000
10	0	-3	30.4	26.4	1.24	0.00000
12	0	-3	32.1	31.5	0.18	0.50000
0	0	-1	89.5	92.5	0.56	0.00000
-9	1	3	51.5	51.2	0.06	0.99140
-5	-1	3	50.4	52.1	0.43	0.49258
-3	-1	3	55.1	57.2	0.50	0.98005
-1	-1	3	32.1	29.3	0.84	0.01844
-5	-1	4	32.6	27.0	1.66	0.48810
-3	-1	4	42.7	46.7	1.09	0.00068
-3	-1	5	38.2	45.8	2.15	0.98709
-1	-1	5	24.5	24.1	0.11	0.49053
-1	-1	2	72.7	77.7	1.05	0.99676
1	-1	1	15.3	14.9	0.16	0.39697
1	-1	2	32.1	32.1	0.00	0.50914
1	-1	3	56.8	62.5	1.35	0.48776
1	-1	4	37.5	39.9	0.69	0.50287
1	-1	5	25.3	26.6	0.44	0.48443
3	-1	5	35.4	45.7	3.02	0.98771
3	-1	4	30.1	30.9	0.25	0.99848
3	-1	3	28.1	22.8	1.67	0.95108
3	-1	2	36.8	31.5	1.52	0.49923
3	-1	1	30.3	34.7	1.37	0.56429
5	-1	1	38.7	38.8	0.03	0.01121
5	-1	2	52.2	52.2	0.00	0.01328
5	-1	3	51.7	49.0	0.67	0.00406
7	-1	1	35.0	33.6	0.41	0.02294
-9	-1	4	35.4	37.3	0.57	0.99811
9	-1	2	44.0	38.6	1.43	0.50651
9	-1	1	36.8	35.9	0.26	0.51621
11	-1	3	32.6	35.5	0.90	0.00038
13	-1	2	37.0	31.8	1.48	0.98893
13	-1	1	42.7	40.0	0.72	0.00210
13	-1	0	50.1	46.6	0.88	0.99055
11	-1	0	47.3	41.3	1.55	0.48016
7	-1	0	78.9	81.8	0.59	0.98928
3	-1	0	66.1	68.0	0.42	0.49792
1	-1	-1	69.8	72.7	0.62	0.01759
5	-1	-1	49.4	47.7	0.42	0.48853
7	-1	-1	56.9	53.6	0.78	0.01352
11	-1	-1	47.3	43.9	0.88	0.49914
11	-1	-2	56.9	48.4	2.00	0.48582
9	-1	-2	45.5	37.7	2.03	0.99632
7	-1	-2	48.1	44.8	0.85	0.98482
5	-1	-2	68.9	65.7	0.67	0.49066
1	-1	-2	74.2	77.7	0.73	0.99676
3	-1	-3	56.1	57.2	0.27	0.98005
5	-1	-3	51.4	52.1	0.19	0.49258
9	-1	-3	52.6	51.2	0.34	0.99140
-10	-2	3	27.1	21.4	1.82	0.96353
-8	-2	3	31.3	27.3	1.23	0.03437
-6	-2	3	35.0	32.4	0.75	0.50190
-2	-2	3	51.1	50.1	0.23	0.00519
-2	-2	4	27.9	29.8	0.60	0.02536
-6	-2	4	27.2	29.2	0.66	0.53376
0	-2	4	26.6	23.3	1.05	0.56142
0	-2	2	50.0	44.5	1.38	0.94102
0	-2	1	61.7	65.0	0.74	0.00283
2	-2	1	51.1	52.7	0.39	0.49021
2	-2	2	60.9	61.1	0.03	0.48574
2	-2	3	41.0	40.3	0.20	0.49094
4	-2	4	31.6	36.9	1.60	0.02218
4	-2	3	42.2	44.0	0.50	0.98658
4	-2	2	20.0	14.6	1.87	0.09743
4	-2	1	15.1	11.8	1.20	0.59228
6	-2	1	61.9	65.1	0.71	0.99637
6	-2	2	59.3	57.7	0.38	0.97422
6	2	3	23.5	21.1	0.79	0.98750
8	-2	3	44.4	46.1	0.45	0.47776
8	-2	2	34.3	35.7	0.41	0.49496
8	-2	1	24.4	21.4	1.00	0.45355
10	-2	1	27.9	29.5	0.52	0.53116
10	-2	3	15.4	15.5	0.04	0.95923
12	-2	2	37.5	40.7	0.92	0.99307
12	-2	1	34.5	35.4	0.28	0.98642
12	-2	0	20.1	14.4	1.99	0.97680
10	-2	0	46.8	45.4	0.38	0.48789
8	-2	0	22.4	18.9	1.18	0.01520
6	-2	0	70.3	66.3	0.84	0.97065
4	-2	0	56.2	59.3	0.74	0.47196
2	-2	0	23.4	25.8	0.83	0.44461
10	-2	-1	27.2	25.7	0.49	0.53845
8	-2	-1	36.3	37.1	0.24	0.03629
6	-2	-1	31.6	22.9	2.63	0.99417
4	-2	-1	47.9	51.9	1.02	0.52024
2	-2	-1	27.3	23.6	1.20	0.01912
0	-2	-1	61.5	65.0	0.78	0.00283
2	-2	-2	43.4	45.2	0.48	0.02631
4	-2	-2	47.8	47.2	0.18	0.47616
8	-2	-2	44.0	45.4	0.37	0.00730
12	-2	-2	24.4	26.8	0.79	0.51194
8	-2	-3	28.4	27.3	0.35	0.03437
6	-2	-3	30.2	32.4	0.69	0.50190

component octahedra. The latter is a description in terms of a shear structure [9] introduced by Magnéli [10] and later developed by Andersson.[11]

The difference between the two structures becomes significant when the distortions of the metal atoms from the centres of the octahedra are considered. These displacements occur predominently along the direction of the *c* axis.

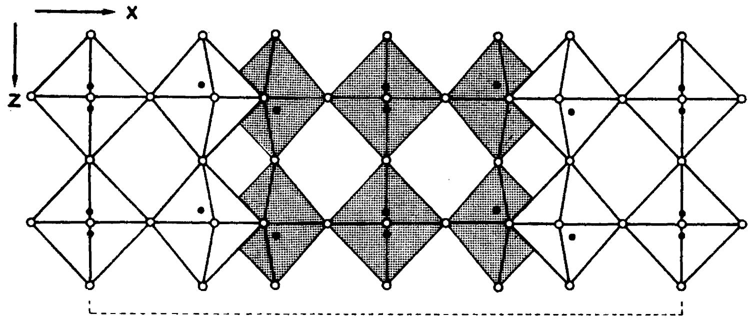


Fig. 2. The structure of V_2MoO_8 presented analogously with those in Fig. 1. In the octahedra containing two dots the metal atoms are situated alternatingly at the two positions in the strings of octahedra running along the line of sight. The dashed line indicates a repeat distance.

It is seen in Fig. 1 that in V_2O_5 all metal atoms *within an ReO_3-type slab* are displaced in the same direction while in $(Mo_{0.3}V_{0.7})_2O_5$ they are shifted pairwise in opposite directions. The reason for this interesting difference between the two structures is not understood and is being further investigated. In both structures the metal atoms *in a pair of octahedra sharing edges* are displaced in opposite directions which, of course, is energetically most favorable from a purely electrostatic point of view.

It is interesting to compare these two structures with that of V_2MoO_8 [12] shown in Fig. 2. Here the slabs of ReO_3 type have a thickness of three octahedra instead of two but the interconnection of the slabs remains the same. *Homologous series* of structures is a term introduced by Magnéli for this type of structural relationship.[10] Considering the offcenter displacements of the metal atoms V_2MoO_8 forms an intermediate between the above-mentioned structures since the displacement within the middle octahedra of each slab goes in both directions; it alternates between $+z$ and $-z$ when going in the direction of the b axis which is therefore doubled (*cf.* Fig. 2). Both types of relative displacement within neighboring octahedra are thus present simultaneously in this structure.

Table 5. Metal oxygen distances.

Atoms	$(Mo_{0.3}V_{0.7})_2O_5$ Coordinates x	y	z	Distance (in Å)	V_2O_5(8) Distance (in Å)	MoO_3(14) Distance (in Å)
M–	0.149	0	0.100			
–O(1)	0.145	0.065	0.493	1.659 (± 18)	1.585	1.671
–O(2)	0.179	–0.448	–0.005	1.733 (± 36)	1.780	1.734
–O(3)	0	0.002	0	1.804 (± 3)	1.878	1.948
–O(2)	0.321	0.052	0.005	2.081 (± 16)	1.878	1.948
–O(2)	0.179	0.552	–0.005	2.094 (± 36)	2.021	2.251
–O(1)	0.145	0.065	–0.507	2.544 (± 18)	2.785	2.332

The $M-O$ distances which are given in Table 5 can be grouped together in three short, two intermediate, and one long bond. There is thus a marked tendency towards five-fold coordination although not as pronounced as in V_2O_5. The range of the $M-O$ distances is seen to be intermediate between those in V_2O_5 and MoO_3. All close O—O distances have normal values ranging from 2.48 ($\pm$ 6) Å (along the shared edge) to 2.97 ($\pm$ 2) Å.

The Nb—O distances in R-Nb_2O_5 as given by Gruehn[6] range from 1.7 to 2.3 Å which indicates a slightly smaller distortion in that structure than in the isostructural $(Mo_{0.3}V_{0.7})_2O_5$.

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REFERENCES

1. Kihlborg, L. *To be published.*
2. Kihlborg, L. and Eick, H. A. *Acta Cryst.* **21** (1966) A 59.
3. Eick, H. A. and Kihlborg, L. *Acta Chem. Scand.* **20** (1966) 722.
4. *IUCr World List of Crystallographic Computer Programs*, 2nd Ed., A. Oosthoek's Uitgevers Mij. N. V., Utrecht 1966.
5. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III.
6. Gruehn, R. *J. Less-Common Metals* **11** (1966) 119.
7. Byström, A., Wilhelmi, K.-A. and Brotzen, O. *Acta Chem. Scand.* **4** (1950) 1119.
8. Bachmann, H. G., Ahmed, F. R. and Barnes, W. H. *Z. Krist.* **115** (1961) 110.
9. Wadsley, A. D. *Rev. Pure Appl. Chem.* **5** (1955) 165.
10. Magnéli, A. *Acta Cryst.* **6** (1953) 495.
11. Andersson, S. *Bull. Soc. Chim. France* **1965** 1088.
12. Eick, H. A. and Kihlborg, L. *Acta Chem. Scand.* **20** (1966) 1658.
13. Hambling, P. G. *Acta Cryst.* **6** (1953) 98.
14. Kihlborg, L. *Arkiv Kemi* **21** (1963) 357.

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