The Crystal Structure of Monoclinic Wolfram Vanadium Oxide, $W_3V_5O_{20}$, an OD Structure Related to R–Nb_2O_5

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The monoclinic ternary phase in the W–V–O system reported by Freundlich has been studied by X-ray diffraction methods. A careful phase analysis indicates a composition close to $W_3V_5O_{20}$ and this is confirmed by the results of the crystal structure determination. The least-squares refinement of the structure resulted in a conventional $R = 0.073$.

The unit cell dimensions are $a = 24.41$ Å, $b = 7.446$ Å, $c = 3.950$ Å, $\beta = 91.03°$ and the space group is $C2/m$. The structure is basicly the same as that of R–Nb_2O_5 and $(Mo_{0.3}V_{0.7})_2O_5$ which are built up of MO_6 octahedra sharing edges and corners as in V_2O_5 although with a different pattern for the off-center displacements of the metal atoms inside the octahedra.

Wolfram and vanadium are partly orderly distributed which gives rise to a superstructure. Two positions are occupied by W and V, respectively, and the third statistically by ($\frac{1}{4}$ W + $\frac{3}{4}$ V) with no indications of order. ESCA measurements and considerations of the M–O bond lengths suggest that wolfram is hexavalent while vanadium is pentavalent in the singly occupied position and tetravalent in the site shared with wolfram.

The structure is an OD structure, since a part of the diffraction spots is diffuse. A model is proposed which explains the partial disorder as due to mistakes analogous to stacking faults.

Introduction

In 1965 Freundlich reported the existence of two previously unknown phases in the W–V–O system (*1*). These were obtained by heating mixtures of WO_3 and V_2O_5 under continuous pumping or by heating mixtures of W, WO_3 and V_2O_5 in sealed silica tubes. One of these phases, with a composition close to $WV_2O_{7.5}$, was obtained below 800°C and was found to possess tetragonal symmetry. The second phase, stable up to 1000°C, was reported to be monoclinic and to have the composition WV_2O_{8-x} with a homogeneity range $0.9 < x \leqslant 1.1$.

The crystal structures of these compounds have been studied by Freundlich, Rimsky, and coworkers in Paris and, independently, by the present authors. A note about the structure of the monoclinic phase has been published by the Paris group (*2*). Our own results for both structures have been briefly communicated elsewhere (*3*) and a full account of our studies of the tetragonal phase has recently appeared (*4*). The structure derived by us for the monoclinic phase, which differs considerably from that published by Mondet et al. (*2*), is presented in full in this article.

Preparation, Stoichiometry and Unit Cell Dimensions

Samples were prepared by heating weighed mixtures of reagent-grade WO_3, V_2O_5 and V_2O_3 in evacuated sealed silica or platinum tubes for several days. The sesquioxide had been prepared by reducing V_2O_5 in a stream of hydrogen.

The powder patterns of the products were recorded in Guinier-Hägg-type cameras using $CuK\alpha_1$ radiation and KCl as internal standard ($a = 6.2919$ Å). Preparations made at 900°C with compositions close to $W_{0.375}V_{0.625}O_{2.50}$ gave a pattern (Table I) which contained only lines indexable on the basis of a monoclinic unit cell with the dimensions given in Table I. The a and b axes are doubled compared with the values originally given by Freundlich (*1*) but agree with those reported by Mondet et al. (*2*). On the other hand, faint additional lines were visible in samples with the following compositions (indicated by x/y and referring to the formula $W_xV_{1-x}O_y$), namely 0.364/2.545, 0.400/2.500, 0.333/2.500 and 0.385/2.457, and hence these were not monophasic. The lattice parameters obtained from these patterns differed by at most 0.3% from those given in Table I and did not give positive

TABLE I

X-Ray Powder Diffraction Data for $W_3V_5O_{20}$—
CuKα_1 Radiation ($\lambda = 1.54051$ Å)

The calculated unit cell parameters are $a = 24.413(\pm 3)$ Å,
$b = 7.446(\pm 2)$ Å, $c = 3.950(\pm 1)$ Å, $\beta = 91.03(\pm 2)°$.
$\Delta = \sin^2 \theta_{obs} - \sin^2 \theta_{calc}$.

I	d_{obs} Å	$\sin^2 \theta_{obs}$ $\times 10^5$	$h\,k\,l$	Δ $\times 10^5$
vw	7.149	1161	1 1 0	−9
m	6.120	1584	4 0 0	−9
vw	5.519	1948	3 1 0	−18
vw	4.086	3554	5 1 0	−6
vs	3.949	3804	0 0 1	+1
vs	3.572	4649	2 2 0	−30
vw	3.453	4976	1 1 1	−19
vw	3.336	5333	$\bar{4}$ 0 1	+25
m	3.302	5443	4 0 1	−42
vw	3.225	5704	$\bar{3}$ 1 1	+1
vw	3.201	5792	3 1 1	−44
m	3.059	6342	8 0 0	−31
s	2.754	7824	6 2 0	−42
s	2.653	8429	$\bar{2}$ 2 1	−9
m	2.433	10025	$\bar{8}$ 0 1	+26
vw	2.378	10496	3 3 0	−32
vw	2.267	11547	$\bar{6}$ 2 1	+11
m	2.248	11753	6 2 1	−49
w	2.040	14254	$\begin{cases} 10\ 2\ 0 \\ 3\ 3\ 1 \end{cases}$	$\begin{matrix} +15 \\ -11 \end{matrix}$
m	1.975	15212	0 0 2	0
vw	1.885	16693	$\overline{11}$ 1 1	+13
s	1.868	17006	$\begin{cases} 4\ 0\ 2 \\ \bar{3}\ 1\ 2 \end{cases}$	$\begin{matrix} +23 \\ -40 \end{matrix}$
w	1.825	17813	$\overline{10}$ 2 1	−8
vw	1.804	18237	10 2 1	−26
vw	1.786	18596	$\bar{5}$ 1 2	+45
m	1.730	19814	$\bar{2}$ 2 2	+11
w	1.687	20847	$\bar{7}$ 1 2	+5
vw	1.668	21337	$\bar{9}$ 3 1	+35
vw	1.626	22455	$\bar{4}$ 4 1	+24
m	1.593	23370	6 2 2	+26
s	1.580	23766	14 2 0	−36
w	1.479	27110	$\begin{cases} 5\ 3\ 2 \\ 8\ 4\ 1 \end{cases}$	$\begin{matrix} -3 \\ -13 \end{matrix}$
vw	1.475	27288	$\overline{14}$ 2 1	−5
vw	1.464	27679	3 5 0	+27

evidence for the existence of an extended homogeneity range. Freundlich did not report any variable cell dimensions but seems to have drawn his conclusion about a variable composition from a failure to detect a second phase in a composition interval.

The density was determined on several apparently monophasic samples by the method of Archimedes using chloroform as an immersion liquid. The mean value $\rho_{obs} = 5.18 \pm 0.03$ g/cm³ was obtained compared with $\rho_{calc} = 5.209$ g/cm³ calculated for a cell content of $16 \times (W_{0.375}V_{0.625}O_{2.50}) = W_6V_{10}O_{40}$. Mondet et al. report a density of $\rho_{obs} = 5.41$ g/cm³ while the value $\rho_{calc} = 5.52$ g/cm³ can be calculated from the stoichiometry and structure they propose with a cell content of $W_6V_{12}O_{42}$. Our investigations thus point to a composition which is somewhat different from that given by Freundlich (1) and assumed in his subsequent structure determination (2).

X-Ray Data

The crystal used in the single crystal studies was selected from a sample with the gross composition $W_{0.40}V_{0.60}O_{2.50}$ which had been heated in an evacuated, sealed platinum tube to 1100°C whereafter the temperature had been gradually lowered to about 940°C over a period of 7 days. The crystal was a black rod with a nearly rectangular cross-section and the dimensions $0.021 \times 0.058 \times 0.011$ mm³ along a, b, and c, respectively.

Weissenberg photographs were recorded of the h0l-h4l and the h6l layer lines using CuKα radiation and multiple film technique. The h5l layer contained no reflections of measurable intensity.

The reflections hkl with $k = 2n$ were all sharp while those with $k = 2n + 1$ were throughout weak and diffuse, being markedly elongated along the bows corresponding to the direction of a^*. About 50 crystals were preliminarily investigated before the final one was selected but all gave the same type of diffuse reflections. The sharp reflections could be indexed on the basis of the subcell with $a' = \frac{1}{2}a$ and $b' = \frac{1}{2}b$. The superstructure indicated by the diffuse reflections is thus associated with a certain degree of one-dimensional disorder.

The relative intensities of the reflections were estimated by means of two calibrated scales, one for the sharp and one for the diffuse spots. The intensity values were corrected for the effect of absorption and the usual Lp correction was applied.

Space Group

The absence of reflections hkl for $h + k = 2n + 1$ indicated a C-centered lattice. Since the h0l reflections were present for all values of l, the possible space groups for the superstructure were $C2$, Cm and $C2/m$.

When only the substructure reflections $h'k'l$ were considered, the same extinction conditions seemed to be valid since reflections with $h' + k' = 2n + 1$

$(h + k = 4n + 2)$ were not visible on the Weissenberg films. A careful check of one of these reflections $(14, 0, 2)$ by means of a single crystal diffractometer revealed, however, that it had an intensity definitely above background but was very diffuse. The apparent absence of these reflections thus did not result from symmetry and will be further discussed below.

Structure Determination

A three-dimensional Patterson function calculated from the observed data clearly demonstrated a close similarity between the present structure and that of $(Mo_{0.3}V_{0.7})_2O_5$ (5). This was also indicated by the unit cell dimensions. The subcell of the present structure $(a' = 12.21$ Å, $b' = 3.713$ Å, $c = 3.950$ Å, $\beta = 91.03°)$ should be compared with the following values for $(Mo_{0.3}V_{0.7})_2O_5$: $a = 11.809$ Å, $b = 3.652$ Å, $c = 4.174$ Å, $\beta = 90.56°$. This latter structure is C-centered which is approximately true also for the substructure of $W_3V_5O_{20}$ as indicated by the weakness of the reflections with $h' + k' = 2n + 1$ (see above).

The superstructure was revealed in the Patterson maps by differences between the heights of peaks which would be identical in the substructure, but no shifts in their positions could be found. It was, therefore, concluded that the superstructure is associated predominantly with the distribution of the two kinds of metal atoms over the available positions.

A substructure with the same positional parameters as in $(Mo_{0.3}V_{0.7})_2O_5$ was assumed and different distributions of the vanadium and wolfram atoms over the metal atom positions in order to form the superstructure were tried by least squares refinement.

The space group of $(Mo_{0.3}V_{0.7})_2O_5$ is $C2$ (the deviation from $C2/m$ is small) (5) and the same symmetry was assumed for the present phase with respect to the superstructure. This gave an asymmetric unit containing four metal atom positions (Fig. 1).

The possible ordered distributions of 1 or 2 W and 3 or 2 V atoms were first tried (the W/V ratio was only very approximately known at this stage). These alternatives did not refine very far and gave unreasonable B values. When mixed W-V scattering factors were used for the positions M(1') and M(1'') (Fig. 1), much better results were obtained. The assignment of $(0.25$ W $+ 0.75$ V) to both these positions resulted in quite reasonable B values. The same result, within the standard deviations, was obtained by a least squares procedure including

refinement of occupancy parameters G for these positions, keeping $G(W) + G(V) = 1$ for both. The refinements also indicated that M(2) is occupied by wolfram atoms only and M(3) exclusively by vanadium atoms. This gives a composition and unit cell content in agreement with the results of the phase analysis and the measured density (see above).

All positions refined under the above assumptions, including those for the oxygen atoms, were pairwise centrosymmetrically related within the limits of the standard deviations. The space group symmetry could therefore be raised to $C2/m$ whereby, for example, the positions M(1') and M(1'') became equivalent. The least-squares procedure continued under this assumption gave quite satisfactory results for the metal atoms. The B values obtained for the oxygen atoms were rather divergent, but were associated with very high standard deviations. This is a phenomenon often encountered in structure determination of heavy metal oxides, especially when photographic data are used. The last few least-squares cycles were performed refining an over-all temperature factor common to all the oxygens. All oxygen positions thus obtained were in complete agreement with the maxima of a difference Fourier map in which the calculated contribution from the metal atoms had been subtracted. The lowest of these oxygen peaks was about three times higher than any maximum in a full-difference synthesis finally computed.

The R value $(R = \Sigma|F_{obs}-F_{calc}|/\Sigma|F_{obs}|)$ finally achieved was 0.073 including all observed reflections. The parameters obtained are given in Table II.
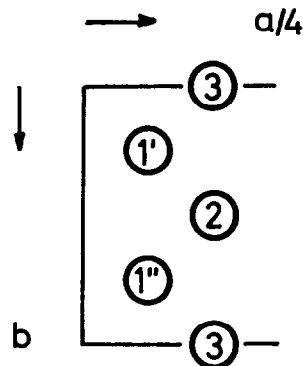

FIG. 1. The numbering of the metal atom positions. 1' and 1'' are nonequivalent in space group $C2$ but symmetry-related (by the mirror planes) in the space group $C2/m$.

TABLE II

FINAL POSITIONAL AND THERMAL PARAMETERS

The standard deviations given within parentheses correspond to the least significant digits. Space group: $C2/m$ (No. 12). Unit cell dimensions: $a = 24.413(3)$ Å, $b = 7.446(2)$ Å, $c = 3.950(1)$ Å, $\beta = 91.03(2)°$. Cell content: 2 $W_3V_5O_{20}$. M(1) = $(W_{1/4}V_{3/4})$, M(2) = W, M(3) = V.

Atom	Point position	x	y	z	B
M(1)	8j	0.0739(2)	0.2494(9)	0.0856(14)	0.49(7)
M(2)	4i	0.1787(1)	½	0.9291(7)	0.24(3)
M(3)	4i	0.1715(4)	0	0.9163(25)	1.61(19)
O(1)	4g	0	0.262(6)	0	
O(2)	4i	0.0902(14)	0	0.026(9)	
O(3)	8j	0.1589(13)	0.255(5)	0.033(9)	
O(4)	4i	0.0886(14)	½	0.036(9)	0.9(5)
O(5)	4i	0.2493(12)	½	0.995(8)	
O(6)	8j	0.0795(13)	0.250(5)	0.536(9)	
O(7)	4i	0.1787(14)	½	0.511(9)	
O(8)	4i	0.1822(14)	0	0.556(10)	

Details of the Calculations

All calculations were performed on computers of the types CD 3600 and IBM 1800. The absorption correction was made with a program of Coppens et al. (6) modified by O. Olofsson and M. Elfström.† The least squares refinement was mainly performed by means of a block diagonal matrix program (SFLS, written by S. Åsbrink‡ and C.-I. Brändén,† modified for IBM 1800 by B. Brandt‡). A full matrix program (LALS, a local version of the program UCLALS by Gantzel, Sparks and Trueblood, modified by R. Liminga, J.-O. Lundgren and C.-I. Brändén†) was also used for a part of the calculations.

HFS scattering factors for unionized atoms (7) were used with the application of the real part of the dispersion correction (8). The weights in the least-squares treatment were calculated according to the expression $w = (50 + |F_{obs}| + 0.008|F_{obs}|^2)^{-1}$. The weight analyses obtained in the last cycle are given in Table III. The observed and calculated structure factors are listed in Table IV.

Description of the Structure

The structure, depicted in Fig. 2, is of the same type as $R-Nb_2O_5$ (9) and $(Mo_{0.3}V_{0.7})_2O_5$ (5). These can be considered to be built up of MO_6 octahedra

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sharing corners and edges as in V_2O_5 but with the metal atoms following a different off-center displacement pattern (5). While there is random distribution of the two kinds of metal atoms in the molybdenum vanadium oxide, the present structure exhibits partial ordering of the wolfram and vanadium atoms which gives rise to a superstructure as mentioned above.

The structure may best be described in terms of octahedra sharing edges and corners to form zigzag strings running in the b direction. These strings are connected by mutual corner-sharing in the c direction which gives rise to layers consisting of octahedra at two levels. The octahedra at one level contain $(W_{1/4}V_{3/4})$ in random distribution while the octahedra at the other level are filled alternately with W and V when going in the b direction.

The double layers are stacked on top of each other with all apical oxygen atoms shared between two layers. [It may be worth mentioning that MoO_3 is composed of octahedra forming the same type of layers which, however, do not share oxygen atoms with each other (10).] The two sides of the double layers are not equivalent and every second layer is rotated 180° around [010] thus bringing like sides of adjacent layers into contact.

Comparison with the Structure Proposed by Mondet et al.

The structure model proposed by Mondet et al. (2) is illustrated in Fig. 3 (which does not indicate

TABLE III

WEIGHT ANALYSIS OBTAINED IN THE LAST CYCLE OF REFINEMENT

$\Delta = |F_{obs}-F_{calc}|$, w = weighting factor. The $w\Delta^2$ values have been normalized.

Interval $|F_{obs}|$	Number of independent reflections	$\overline{w\Delta^2}$	Interval $\sin\theta$	Number of independent reflections	$\overline{w\Delta^2}$
0–87	32	0.723	0.000–0.464	58	1.646
87–99	32	0.878	0.464–0.585	37	0.627
99–109	29	0.577	0.585–0.669	43	0.599
109–128	32	0.720	0.669–0.737	32	1.446
128–141	31	1.472	0.737–0.794	33	0.868
141–163	27	0.669	0.794–0.843	27	0.419
163–190	30	1.333	0.843–0.888	37	1.081
190–233	33	0.974	0.888–0.928	21	1.100
233–297	31	1.080	0.928–0.965	21	0.577
297–490	40	1.420	0.965–1.000	8	1.386

TABLE IV

COMPARISON BETWEEN OBSERVED AND CALCULATED STRUCTURE AMPLITUDES

The table gives h, k, l, $|F_{obs}|$ and $|F_{calc}|$.

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-28 0 0 199 229   -25 1 0 121 127   -19 1 3  79  78   18 2 2 276 256   -7 3 2 134 123   24 4 1 109 131
-20 0 0 291 318   -23 1 0 101  89   -15 1 3 102 101   26 2 2 218 234   -5 3 2 156 138  -24 4 2 179 163
-16 0 0 175 179   -19 1 0 141 130   -13 1 3 122 110   -22 2 3 178 151   -1 3 2  62  65  -20 4 2  86  88
-12 0 0 440 491   -17 1 0 156 140    -7 1 3 116 118   -18 2 3 284 272    3 3 2 142 139  -16 4 2 288 290
 -8 0 0 447 498   -13 1 0  98  88    -5 1 3 101  96   -10 2 3 327 320    7 3 2 119 130   -8 4 2 345 331
 -4 0 0 231 214   -11 1 0 169 163    -1 1 3  99  94    -6 2 3 181 179    9 3 2 105  99   -4 4 2 214 223
-28 0 1 191 201    -9 1 0 113 116     1 1 3 133 123    -2 2 3 279 277   11 3 2 151 148    0 4 2 305 314
-24 0 1 123 103    -5 1 0 130 148     3 1 3  59  66     2 2 3 260 261   15 3 2  73  81    4 4 2 359 358
-20 0 1 181 170    -3 1 0 128 168     7 1 3 136 117    10 2 3 277 287   17 3 2 123 133   12 4 2 351 372
-16 0 1 283 277   -27 1 1 116 108     9 1 3 105 106    18 2 3 184 199   21 3 2 135 120   16 4 2 133 132
-12 0 1 168 174   -25 1 1 109 112    13 1 3  64  83    22 2 3 101 104   23 3 2  95  86   20 4 2 209 174
 -8 0 1 357 394   -21 1 1  87  81    15 1 3 126 121   -18 2 4 230 230   25 3 2 125 124   24 4 2 196 202
 -4 0 1 148 136   -19 1 1 135 142    21 1 3  96 103   -10 2 4 240 226   -21 3 3  57  71  -20 4 3  76  75
  0 0 1 470 552   -17 1 1  95  94    23 1 3  89  93    -6 2 4 204 200   -19 3 3  95  99  -12 4 3 171 159
  4 0 1 369 359   -13 1 1 134 130   -15 1 4  93 107    -2 2 4 164 154   -15 3 3  72  78   -8 4 3 153 135
  8 0 1 193 159   -11 1 1 149 144   -13 1 4  79  84     2 2 4 247 248   -13 3 3 100  95   -4 4 3 303 289
 12 0 1 419 462    -9 1 1  58  53    -9 1 4  89  84    10 2 4 222 235    -7 3 3 138 119    4 4 3 248 286
 20 0 1 253 246    -7 1 1  73  79    -7 1 4 109 113    14 2 4  87  95    -5 3 3 103  91    8 4 3 152 143
 24 0 1 162 152    -5 1 1 159 161    -5 1 4  64  59   -27 3 0  78  67    -1 3 3  95  94   16 4 3 190 202
 28 0 1 146 146    -3 1 1 139 125    -1 1 4 123 113   -25 3 0 107 124     1 3 3 124 114  -12 4 4 164 174
-28 0 2 178 174     1 1 1 124 119     1 1 4  94 104   -23 3 0  88  84     7 3 3 104 109   -4 4 4 253 242
-24 0 2 210 180     3 1 1 141 164     3 1 4  70  77   -19 3 0 142 128     9 3 3 105 100    4 4 4 193 196
-20 0 2 140 103     5 1 1  90  99    13 1 4 100 106   -17 3 0 130 129    13 3 3  97  77    8 4 4 169 185
-16 0 2 354 338     9 1 1 125 142    15 1 4  93 105   -13 3 0  89  86    15 3 3 126 117   12 4 4 126 114
 -8 0 2 397 407    11 1 1 123 141   -26 2 0 239 241    -9 3 0 140 111    17 3 3 122 111  -22 6 0 212 203
 -4 0 2 275 270    15 1 1 165 146   -22 2 0 270 262    -5 3 0 133 153    21 3 3 105  99  -18 6 0  86  89
  0 0 2 399 421    17 1 1  86  91   -18 2 0 109 105   -27 3 1 104 102   -15 3 4 107 101  -14 6 0 304 327
  4 0 2 409 446    19 1 1 115 115   -14 2 0 461 480   -25 3 1 103 110   -13 3 4  79  85   -6 6 0 353 289
 12 0 2 454 454    23 1 1 109 110   -10 2 0  96  76   -21 3 1  74  72    -9 3 4  79  78  -22 6 1 211 220
 16 0 2 182 157    25 1 1  70  71    -6 2 0 355 430   -19 3 1 147 140    -7 3 4 109 111  -14 6 1 231 250
 20 0 2 226 196    29 1 1  91  75    -2 2 0 402 403   -17 3 1  94  90    -1 3 4 102 112  -10 6 1 167 185
 24 0 2 247 229   -27 1 2 102 112   -30 2 1 167 176   -13 3 1 125 126     1 3 4  92  96   -6 6 1 135 118
-24 0 3 185 211   -25 1 2 108 108   -26 2 1 106 108   -11 3 1 134 132     5 3 4  67  78   -2 6 1 278 282
-20 0 3 104  86   -21 1 2 115 122   -22 2 1 275 278    -7 3 1  80  84     7 3 4 101 114    6 6 1 279 233
-16 0 3 271 244   -19 1 2  83  79   -18 2 1  89  95    -5 3 1 132 142    13 3 4 101  99   10 6 1 103  97
-12 0 3 234 181   -15 1 2 158 138   -14 2 1 333 344    -3 3 1 106 115    15 3 4  96 102   14 6 1 216 216
 -8 0 3 184 152   -13 1 2 121 102   -10 2 1 320 267     1 3 1 103 105   -28 4 0 178 205   18 6 1 148 151
 -4 0 3 343 341   -11 1 2 129 123    -6 2 1 134 116     3 3 1 134 153   -20 4 0 248 273  -18 6 2 173 142
  4 0 3 335 334    -7 1 2 178 151    -2 2 1 350 420     5 3 1  76  77   -16 4 0 152 153  -14 6 2 225 211
  8 0 3 175 192    -5 1 2  69  65     2 2 1 308 288     9 3 1 118 134   -12 4 0 376 368  -10 6 2 286 258
 12 0 3 263 260    -3 1 2 165 155    10 2 1 145 141    11 3 1 129 127    -8 4 0 418 377   -2 6 2 284 321
 16 0 3 268 231    -1 1 2 154 138    18 2 1 304 292    15 3 1  98  91    -4 4 0 179 145    6 6 2 203 220
 24 0 3 192 224     3 1 2 129 111    14 2 1 194 191    17 3 1 143 133   -24 4 1  89  94   10 6 2 187 197
-16 0 4 157 152     7 1 2 150 159    22 2 1 111 117    19 3 1  98  91   -20 4 1 174 152   14 6 2 133 138
-12 0 4 212 192     9 1 2  97  91    26 2 1 230 248    23 3 1 124 109   -16 4 1 246 239   18 6 2 199 203
 -4 0 4 268 275    11 1 2 152 140   -22 2 2 314 280    25 3 1 113 105   -12 4 1 142 134  -10 6 3 276 246
  4 0 4 229 221    13 1 2 130 133   -18 2 2 205 185   -25 3 2  66  76    -8 4 1 358 328   -6 6 3 139 123
  8 0 4 210 210    17 1 2  98  89   -14 2 2 324 296   -21 3 2 102  99    -4 4 1  96 101   -2 6 3 198 209
 12 0 4 130 129    21 1 2 134 132   -10 2 2 336 356   -19 3 2 135 120     0 4 1 401 404    2 6 3 176 194
 16 0 4 225 223    23 1 2  74  73    -2 2 2 446 471   -15 3 2  67  74     8 4 1 159 143   10 6 3 205 221
 -4 0 5 165 183    25 1 3 119 106     2 2 2 122 104   -13 3 2 151 136    12 4 1 367 369
  0 0 5 172 154   -21 1 3 119 106     6 2 2 328 295   -11 3 2 103  93    20 4 1 241 219
-27 1 0  79  71                      10 2 2 308 271
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the suggested disorder mechanism). It is seen that it differs considerably from the results obtained in the present study.

We have made a trial least-squares refinement of this model using our own X-ray data (sharp reflections only). This refinement gave an interesting result, viz., it converged and yielded an R value of 0.11, even lower than the value R = 0.12 reported by Mondet et al. (2). Some of the positions were shifted very much (up to 0.8 Å) from the starting values (2) but the resulting structure was still fundamentally different from our model. Some interatomic distances were improbably short (e.g., V–V 1.8 Å) and the temperature factors were rather
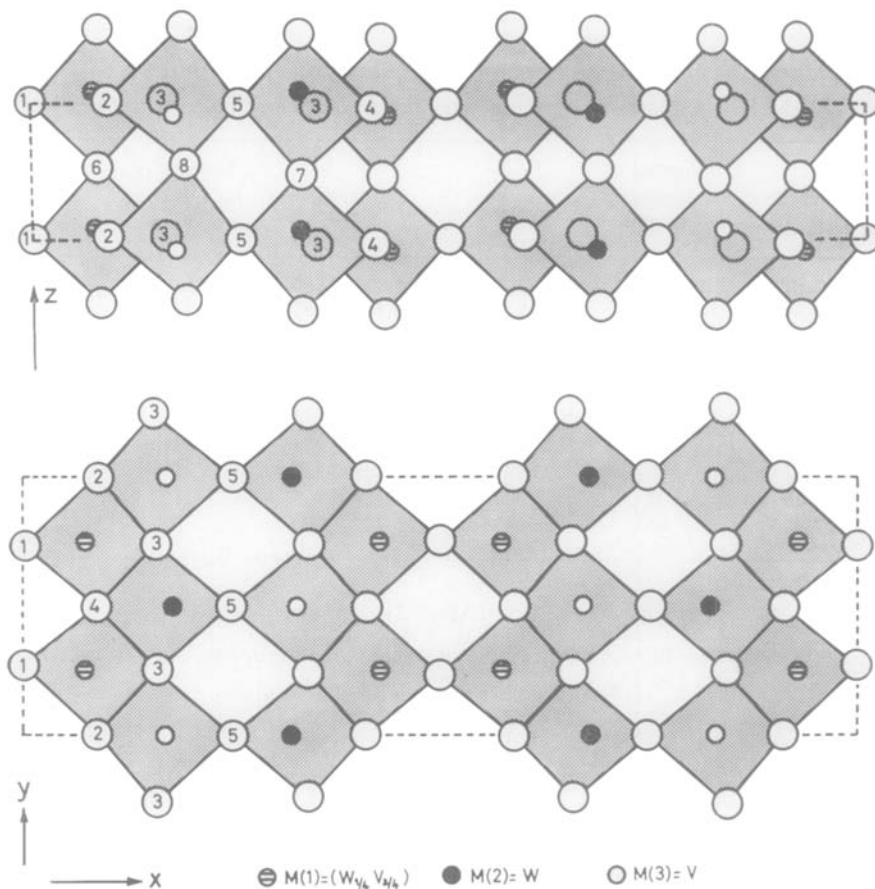
FIG. 2. The structure of $W_3V_5O_{20}$ seen in two projections. Small circles = metal atoms, large circles = oxygen atoms.
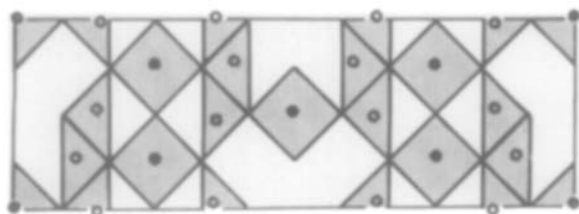

FIG. 3. The structure of WV_2O_7, as proposed by Mondet et al. (2) viewed along [001]. Open circles = vanadium atoms (inside triangular bipyramids), filled circles = wolfram atoms (inside octahedra).

unsatisfactory, ranging from -1.5 to $+1.9$ for the metal atoms. The B values reported by Mondet et al. range from -0.4 to $+1.8$ for the metals and from -0.7 to $+8.3$ Å^2 for the oxygens.

Interatomic Distances

Interatomic distances are listed in Table V. The M–O bond lengths indicate that the coordination

is far from regular. The distortion arises mainly from off-center displacements of the metal atoms within the octahedra. It is seen from the table that the range for the M–O distances, and hence the displacement, is smallest for M(1) and largest for M(3). The shortest bond length in the last case, M(3)–O(8) 1.45 Å, seems rather short, however, since the shortest V–O distances reported to our knowledge are 1.52($\pm$5) Å in NaV_2O_5, (11), 1.56($\pm$5) Å in $Pb_xV_2O_5$ (12) and 1.585($\pm$4) Å in V_2O_5 (13). The position obtained for O(8) also brings it unusually close to O(5) [separation 2.41($\pm$5) Å]; therefore, we believe that the parameters calculated for this atom are slightly in error. A reduction of its the z coordinate by 3σ brings the M(3)–O(8) distance close to the V_2O_5 value and makes the O(5)–O(8) separation more probable.

All other O–O separations are larger than 2.65 Å with the exception of O(2)–O(3) (2.54 Å), O(3)–O(4) (2.50 Å), O(3)–O(8) (2.54 Å) and O(5)–O(7) (2.55 Å). The first two correspond to edges shared between octahedra and such edges are normally short.

Oxidation States

The question immediately presents itself why the two kinds of metal atoms segregate into an ordered distribution over two of the positions but remain apparently randomly distributed in the third site. There are some indications that this phenomenon is associated with the valence states of the metal atoms in the different positions.

Consideration of the chemical behaviour of V(V) and W(VI) makes probable that vanadium is preferentially reduced in the present compound. Support for this view has been obtained from measurements of photoelectron energies according to the ESCA method (*14*). While a single distinct maximum was obtained from the WN_{VII} ($4f_{7/2}$) level, the peak corresponding to VL_{III} ($2p_{3/2}$) was clearly split, suggesting the presence of vanadium in two different valence states (*15*).

Sixfold coordination around pentavalent vanadium is generally very distorted, as for example in V_2O_5 where the V–O bonds range from 1.58 to 2.78 Å (*13*). V(IV), on the other hand, is often found in a more regular octahedral coordination, as for example in VO_2 for which the corresponding range is 1.76–2.06 Å (*16*).

A slightly more quantitative basis for the comparison between the vanadium coordination in this and other structures can be attained by making bond number calculations. This has been done by Evans for a series of vanadium oxides, oxide hydroxides and vanadates (*17*). He used Pauling's formula, $\log n = (d_1 - d_n)/k$, where d_1 and k are empirical constants, for the calculation of the bond number n for a bond of distance d_n. The sum of the bond numbers for a particular cation should then be a rough measure of its valence. Using the values $d_1 = 1.81$ Å (the single bond V–O distance) and $k = 0.78$, Evans obtained fairly good agreement between the *observed* (calculated with the above formula) and *expected* (from the stoichiometry) values for Σn.

This formula, applied to the present structure (with use of the above values for d_1 and k), gives $\Sigma n = 4.28$ for M(1) and $\Sigma n = 5.35$ for M(3). Without paying too much attention to the absolute magnitudes of these values, they may be compared with the following, calculated from recent structural data: $V^{IV}O_2$ (*16*) $\Sigma n = 4.33$, $V^{IV}OSO_4$ (*18*) $\Sigma n = 4.21$, $V_2^V O_5$ (*13*) $\Sigma n = 5.26$. Therefore, it seems reasonable to assume that M(3) is occupied by V(V) whereas V(IV) prefers the position M(1). A more descriptive formula for the compound would then be $(W_{1/4}^{VI} V_{3/4}^{IV})_2 W^{VI} V^V O_{10}$.

The M–O bond lengths around M(1) agree rather well with the W–O distances in WO_3. The random distribution of the two kinds of metal atoms in this position may thus be explained by the similar coordination requirements of V(IV) and W(VI). A further question then arises, namely why position M(2) is occupied by wolfram exclusively. This cannot be answered by the same type of arguments. It is probable that the conditions governing the distribution of the metal atoms are more complicated and that the detailed electronic structure plays an important role.

Order-Disorder Character

As discussed above, there are no indications of an ordered distribution of the wolfram and vanadium atoms in position M(1). Apart from this there are frequent mistakes in the periodicity of the structure, as indicated by the diffuseness of the superstructure reflections. This partial disorder will be discussed below.

There is no evidence for mistakes in the periodicity along b and c since all reflections are sharp in directions perpendicular to a^*. Because these are the directions of infinite extension of the double layers of octahedra, it seems reasonable to assume that these layers constitute strictly ordered units in the structure [disregarding the disorder in M(1)]. Some further arguments can be put forward in support of this.

It seems reasonable that the forces governing the ordering of the metal atoms should be dependent on the distances between these atoms and should be stronger the shorter these distances are. Accordingly, the tendency to mistakes should be smallest within the zig-zag rows of octahedra—and thus in the b direction—since these contain the shortest M-M separations in the structure (cf. Table V). The metal–metal distances are considerably longer in the c direction so the same arguments cannot be used in that case. As is evident from Fig. 2 and Table V, however, the off-center displacement of the metal atoms has its largest component in this direction. The magnitude of this displacement is rather different for the three metal positions which may favour a strictly ordered arrangement.

It may thus be assumed that the observed occurrence of mistakes along a is caused by faults in the stacking sequence of the double layers. The stacking faults can be of two types (here designated I and II) differing with respect to the mutual orientation of the two adjacent layers at the fault. These are schematically illustrated in Fig. 4. Mistake I

TABLE V

INTERATOMIC DISTANCES IN Å UNITS

Standard deviations in the last digits are given within parentheses.

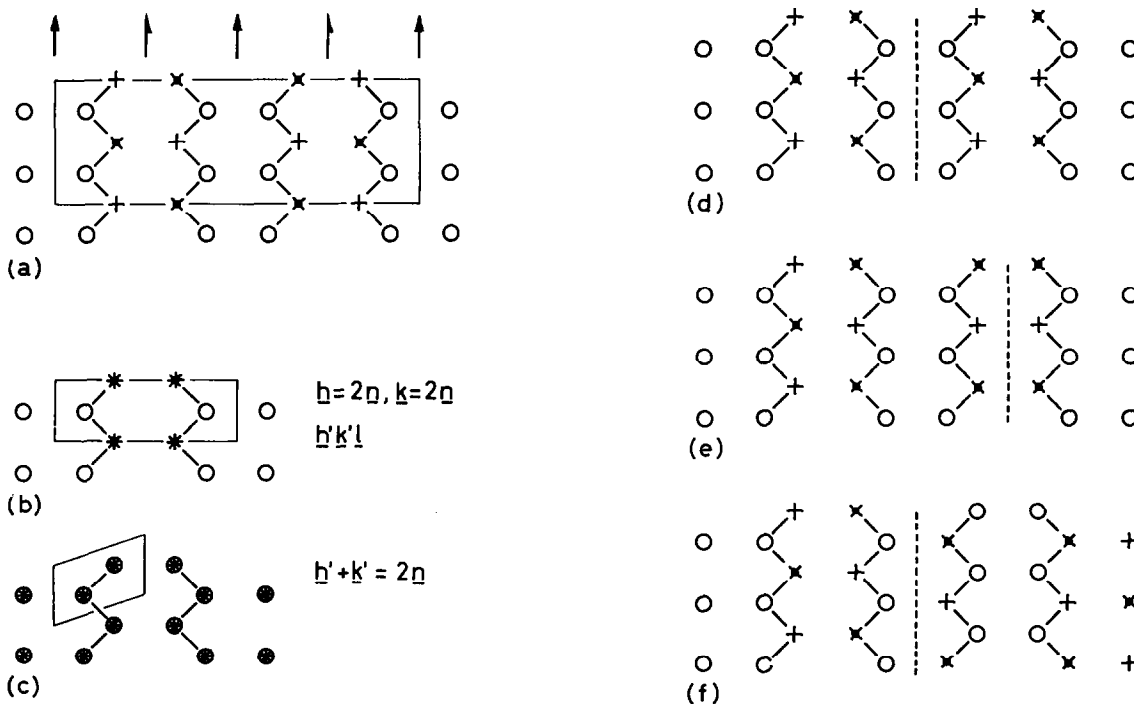|						
M(1)–M(3)		3.103(8)		M(1)–O(6)		1.782(35)
–M(2)		3.235(5)		–O(1)		1.831(5)
–M(1)	~ [100]	3.658(9)		–O(4)		1.910(9)
–M(1)	[010]	3.714(12)		–O(2)		1.914(10)
–M(1)	[010]	3.731(12)		–O(3)		2.089(31)
–M(1)	[001]	2 × 3.950(1)		–O(6)		2.177(35)
M(2)–M(1)		2 × 3.235(5)		M(2)–O(7)		1.651(34)
–M(3)	~ [100]	3.696(9)		–O(5)		1.739(30)
–M(3)	[010]	2 × 3.727(1)		–O(3)	2 × 1.931(33)	
–M(2)	[001]	2 × 3.950(1)		–O(4)		2.248(35)
				–O(7)		2.299(34)
M(3)–M(1)		2 × 3.103(8)		M(3)–O(8)		1.451(39)
— –M(2)	~ [100]	3.696(9)		–O(5)		1.957(31)
–M(2)	[010]	2 × 3.727(1)		–O(3)	2 × 1.981(34)	
–M(3)	[001]	2 × 3.950(1)		–O(2)		2.040(35)
				–O(8)		2.536(39)

FIG. 4. The stacking faults proposed to explain the presence of diffuse reflections. Only metal atom positions are indicated, those belonging to the same double layer have been connected by full lines. o = M(1), X = M(2), + = M(3). The axis a is horizontal, b vertical. (a) The periodic structure. The unit cell is outlined. (b) The superposition structure corresponding to $h = 2n$ and $k = 2n$. (c) The superposition structure corresponding to $h' + k' = 2n$ ($h' = h/2$, $k' = k/2$). The primitive (not the centered) unit cell is indicated. (d) Mistake of type I' (at the hatched line, see text). (e) Mistake of type I''. (f) Mistake of type II, implying a pure translation between two adjacent layers. Superposition structure as in (c).

implies a translation $\frac{1}{2}b$. A pure rotation axis is, thereby, changed into a screw axis (I') or the reverse (I") depending on at which junction the fault occurs (Fig. 4d and e). The superposition structure corresponding to the reflections with both h and k even ($h' = \frac{1}{2}h$, $k' = \frac{1}{2}k$) is left unaffected by this mistake (Fig. 4b) which means that these reflections should remain sharp. This is in accordance with the observations, except that reflections with $h' + k' = 2n + 1$ were found to be diffuse (see above). All these latter reflections have very low $|F_{calc}|$ values since the scattering power contributing to their intensities is $\frac{1}{2}(f_W + f_V) - (\frac{1}{4}f_W + \frac{3}{4}f_V) = \frac{1}{4}(f_W - f_V)$ and only a few could be expected to be detectable on the Weissenberg films even if they had been sharp. Their diffuseness, revealed by a diffractometer (see above), is thus the reason for their apparently systematic absence on the films. This diffuseness, however, can only be explained by mistake II which implies that two adjacent layers are related by a simple translation instead of the normal 180° rotation (Fig. 4f). The superposition structure corresponding to $h' + k' = 2n$ (the simple R–Nb_2O_5 type substructure, Fig. 4c) is invariant for this mistake so these reflections remain sharp whereas all others should become diffuse.

Although mistakes of type II can thus account for all the observed diffuseness of the reflections, it seems likely from a structural point of view that also faults of type I should be present. A detailed study of the widths of the reflections, which could probably give more information about this matter, has not been made in the present investigation.

Acknowledgments

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