

## The Structure of $V_9Mo_6O_{40}$ Determined by Powder Neutron Diffraction\*

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The crystal structure of  $V_9Mo_6O_{40}$  has been determined by Rietveld profile analysis of neutron powder diffraction data. The structure is a monoclinically distorted variant of  $Nb_3O_7F$  (space group  $C2$ ) consisting of  $ReO_3$ -type slabs three octahedra thick connected by edge sharing of component octahedra. The octahedra are considerably distorted due to off-center displacement of the metal atoms. Metal–oxygen bond lengths conform with those of similar compounds. © 1989 Academic Press, Inc.

### Introduction

Oxides of vanadium, molybdenum, and tungsten have been extensively investigated because they form ideal host structures for the reversible insertion of atomic or molecular guest species (1, 2). While  $MoO_3$  and  $V_2O_5$  possess layered structures

(3, 4),  $WO_3$  crystallizes into an  $ReO_3$ -type structure (5, 6). Most of the known ternary oxides crystallize into  $ReO_3$ -related structures defined by different shear mechanisms (7), providing multiple sites for the intercalated materials.

We have recently investigated the hydrogen insertion chemistry of the  $V_2O_5$ – $MoO_3$  system (8). Our studies revealed that a single phase could only be obtained close to the composition  $V_9Mo_6O_{40}$ , or  $V_{1.8}Mo_{1.2}O_8$ , in agreement with previous results (9, 10). The structure of a closely related phase,  $V_2MoO_8$ , has been determined by Eick and

\* Neutron scattering experiments were carried out at the National Institute of Standards and Technology (NIST) and at the Institut Laue-Langevin (ILL), Grenoble, France.

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Kihlberg (11) using single-crystal X-ray diffraction techniques. Their studies indicated that the structure is isotypic with  $\text{Nb}_3\text{O}_7\text{F}$ , containing corner- and edge-shared octahedra. They also suggested a possibility of one-dimensional disorder, leading to the doubling of the  $b$  axis. We have carried out the powder neutron diffraction studies on  $\text{V}_9\text{Mo}_6\text{O}_{40}$  prepared under lengthy annealing to determine if any long-range ordering among the metal atoms or oxygens can be detected.

## Experimental

The sample was synthesized as described earlier (8) by heating a stoichiometric mixture of  $\text{V}_2\text{O}_5$  and  $\text{MoO}_3$  at 870 K and was annealed in air at 820 K for a week. The X-ray powder diffraction pattern of the sample could be completely indexed on a monoclinic cell with  $a = 19.388(9)$ ,  $b = 3.628(3)$ ,  $c = 4.123(4)$  Å and  $\beta = 90.6(1)^\circ$ . Chemical analysis of the samples, as determined by dissolution in a known excess of 0.05 M ammonium ceric sulfate and subsequent potentiometric back-titration, confirmed the formulation to be  $\text{V}_9\text{Mo}_6\text{O}_{40}$ .

Powder neutron diffraction data from  $\text{V}_9\text{Mo}_6\text{O}_{40}$  were collected at room temperature using the five-detector powder diffractometer at the National Institute of Standards and Technology (NIST) reactor (12). A vanadium can of 8 mm diameter was used as the sample container. Monochromated thermal neutrons with  $\lambda = 1.548$  Å were used to record the diffraction profile in the  $2\theta$  range  $12^\circ \leq 2\theta \leq 125^\circ$  in steps of  $0.05^\circ$ . Data were also collected for the same sample at 4 K on a constant wave length ( $\lambda = 1.909$  Å) diffractometer (D1A) at the Institut Laue-Langevin from  $2\theta = 10^\circ$  to  $136^\circ$  with a step size of  $0.05^\circ$ .

The data for the two temperatures were analyzed by the Rietveld method (13) with a program (14) modified to adapt to a five de-

tector diffractometer design and to allow the refinement of background intensity.

The neutron scattering lengths employed in the refinement were  $-0.0382$ ,  $0.6950$ , and  $0.5805 \times 10^{-12}$  cm respectively for V, Mo, and O. Approximate values of the background parameters were obtained from parts of the pattern that contained no contribution from any Bragg reflection. During the last cycles of refinement all structural and profile parameters were refined simultaneously.

## Structure Refinement

Initial unit cell and positional parameters were based on Eick and Kihlberg's model of  $\text{V}_2\text{MoO}_8$  (space group  $C2$ ) (11); vanadium and molybdenum atoms were randomly distributed over the two available sites. The background was fitted using a polynomial function containing up to four parameters. A Gaussian peak shape was found to be adequate to fit the observed profile. Preliminary refinements involved scale factor, zero point error, cell constants, and profile parameters. Since the cell possesses a low symmetry, one of the  $y$  coordinates (in our case  $O4$ ) was fixed to define the  $y$  coordinate of the origin. As vanadium is almost invisible to neutrons due to its very small coherent scattering cross section, only Mo atom positions were included in the refinement. Refinement of the starting values led to small shifts in  $x$  and  $z$  coordinates for all the atoms, but large oscillations about mean positions in the  $y$  direction. Holding  $y$  coordinates at their average values, the refinement yielded an agreement index,  $R_{wp}$ , of 32%. By considering, first, an overall temperature factor and then converting to variation of individual temperature factors, it converged to the agreement factors summarized in Table I. Table II lists the positional parameters, temperature factor, and occupancy factor

TABLE I

RIETVELD REFINEMENT RESULTS FOR V<sub>9</sub>Mo<sub>6</sub>O<sub>40</sub><sup>a</sup>

Space group	C <sub>2</sub> <sup>3</sup> -C2
Unit cell parameters	
<i>a</i> (Å)	19.3611(7)
<i>b</i> (Å)	3.6250(1)
<i>c</i> (Å)	4.1215(2)
$\beta$ (°)	90.617(3)
Peak shape used	Gaussian
Number of reflections	266
<i>R</i> <sub>I</sub> (intensity)	9.19
<i>R</i> <sub>P</sub> (profile)	6.77
<i>R</i> <sub>WP</sub> (weighted profile)	8.74
<i>R</i> <sub>E</sub> (estimated)	6.09
<i>N</i> - <i>P</i> + <i>C</i>	3241

<sup>a</sup>  $R_I = \sum |I_{\text{obs}} - I_{\text{calc}}| / \sum I_{\text{obs}}$ ;  $R_P = \sum |Y_{\text{obs}} - Y_{\text{calc}}| / \sum Y_{\text{obs}}$ ;  $R_{WP} = \sqrt{\sum w [Y_{\text{obs}} - Y_{\text{calc}}]^2 / \sum w [Y_{\text{obs}}]^2}$ ; and  $R_E = \sqrt{(N - P + C) / \sum w [Y_{\text{obs}}]^2}$ . *I* is the integrated Bragg intensity, *Y* is the number of counts at angle 2*θ*, *w* is the weight, and *N* - *P* + *C* is the number of observations minus the number of variables plus the number of constraints.

for the various atoms. Table III gives some selected bond distances and angles. The agreement between observed and calculated profiles is shown in Fig. 1.

Refinements were also attempted in the alternative space groups *Cm* and *C2/m*. the space group *Cm* resulted in considerable

TABLE II

POSITIONAL PARAMETERS AND OCCUPANCY AND TEMPERATURE FACTORS FOR V<sub>9</sub>Mo<sub>6</sub>O<sub>40</sub><sup>a</sup>

Atom	Site	Occupancy			<i>B</i> (Å <sup>2</sup> )	
		factor <sup>b</sup>	<i>x</i>	<i>y</i>		
<i>M</i> (1)	4c <sup>d</sup>	0.314(7) <sup>c</sup>	0.0001(8)	0.026(11)	0.090(3)	2.7(3)
<i>M</i> (2)	4c	0.286 <sup>c</sup>	0.1856(6)	0.026(16)	0.082(3)	2.0(3)
O(1)	4c	1.0	0.0987(2)	0.026(5)	0.002(1)	1.2(1)
O(2)	4c	1.0	0.2080(2)	0.526(5)	0.999(1)	0.5(1)
O(3)	4c	1.0	0.1885(2)	0.033(6)	0.493(1)	1.1(1)
O(4)	2b	0.5	0.0	0.0698	0.5	2.8(2)
O(5)	4c <sup>d</sup>	0.5	0.9994(7)	0.528(8)	0.069(2)	1.2(2)

<sup>a</sup> Cell content: V<sub>3.6</sub>Mo<sub>2.4</sub>O<sub>16</sub>.

<sup>b</sup> Equal (for fully occupied lattice sites) to the ratio of the multiplicity of the position (special or general) to the multiplicity of the general position (13).

<sup>c</sup> Sum of metal site Mo occupancy factors constrained by the chemical composition.

<sup>d</sup> disorder about (2a).

shifts and large estimated standard deviations for the positional parameters, and hence was rejected. Space group *C2/m* yielded a reasonable *R* value (*R*<sub>WP</sub> = 10.75%), but the thermal factors for *M1* and *O5* (-1.8 and 5.7) were unrealistic. Also, in space group *C2* disordering is essential in *M1* and *O5* sites, as suggested by Eick and Kihlberg (9); attempts to place them in special positions led to high temperature factors.

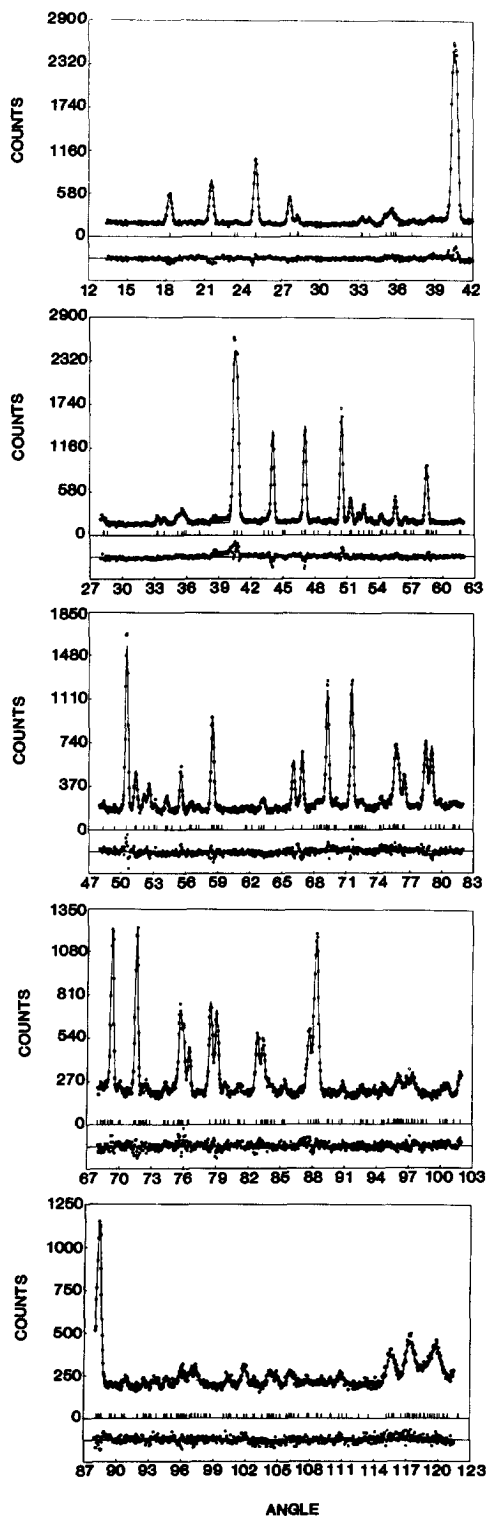
The refinement of the low temperature data was also successful only in the space group *C2* with the agreement factors *R*<sub>I</sub> = 11.25, *R*<sub>P</sub> = 9.47, *R*<sub>WP</sub> = 13.01, and *R*<sub>E</sub> = 8.92. There was no significant change in the structural parameters as well as in the metal coordination with temperature and the data is omitted from further discussion.

TABLE III

SELECTED INTERATOMIC DISTANCES AND ANGLES

	V <sub>9</sub> Mo <sub>6</sub> O <sub>40</sub>	V <sub>2</sub> Mo <sub>8</sub>
<i>M1</i> - <i>O5</i>	1.809(48), 1.821(48) <sup>a</sup>	1.653(39), 1.732(38) <sup>a</sup>
- <i>O4</i>	1.704(12)	1.701(15)
- <i>O1</i>	1.943(15)	1.969(11)
- <i>O1'</i>	1.947(15)	1.972(11)
- <i>O5'</i>	1.919(46), 1.931(45) <sup>a</sup>	2.065(38), 2.000(39) <sup>a</sup>
- <i>O4'</i>	2.431(12)	2.453(4)
<i>M2</i> - <i>O3</i>	1.684(13)	1.644(11)
- <i>O1</i>	1.712(12)	1.715(11)
- <i>O2'</i>	1.894(53)	1.873(29)
- <i>O2</i>	1.900(53)	1.941(29)
- <i>O2''</i>	2.095(12)	2.096(11)
- <i>O3'</i>	2.441(14)	2.475(11)
O-O distances		
<i>O1</i> - <i>O2</i>	2.786(14)	
<i>O1</i> - <i>O3</i>	2.746(7)	
<i>O1</i> - <i>O4</i>	2.810(5)	
<i>O1</i> - <i>O5</i>	2.654(21); 2.664(21) <sup>a</sup>	
<i>O2</i> - <i>O3</i>	2.769(13)	
<i>O4</i> - <i>O5</i>	2.432(21)	
Angles (°)		
<i>O1</i> - <i>M1</i> - <i>O5</i>	89.8(1); 89.9(1) <sup>a</sup>	
<i>O1</i> - <i>M1</i> - <i>O1'</i>	158.4(6)	
<i>O1</i> - <i>M1</i> - <i>O4</i>	100.6(7)	
<i>O4</i> - <i>M1</i> - <i>O5</i>	91.2(9); 83.6(9) <sup>a</sup>	
<i>O1</i> - <i>M2</i> - <i>O2</i>	100.8(20)	
<i>O1</i> - <i>M2</i> - <i>O3</i>	79.5(10)	
<i>O2</i> - <i>M2</i> - <i>O3'</i>	115.0(7)	

<sup>a</sup> Uncertainties arising from the ambiguities in *O5* positions.



## Discussion

The structural parameters of  $V_9Mo_6O_{40}$  are very close to those of  $V_2Mo_8$  (11). The present neutron diffraction study confirms that space group  $C2$  is the most likely for our phase. The structures can both be regarded as that of one of the members of the homologous series  $M_nO_{3n-1}$  ( $n = 3$ ), consisting of blocks of  $ReO_3$ -type slabs three octahedra thick that extend infinitely in the  $bc$  plane; these blocks are interconnected by edge sharing between component octahedra.

The distortion of the octahedral coordination around  $M1$  and  $M2$  is evident (Table III) from the large variations in the metal-oxygen distances. As in  $V_2Mo_8$  and many other vanadium and molybdenum oxides, the off-center displacement of metal atoms results in shortening two and lengthening two other  $M-O$  bonds. A schematic representation of the structure shows the displacement of the metal atoms (Fig. 2).

A comparison of the bond distances for  $V_9Mo_6O_{40}$  and  $V_2Mo_8$  is shown in Table III. While the  $M2$  environment (edge-shared octahedral unit) remains the same, the distortion around  $M1$  (corner-shared octahedra) is considerably lower in  $V_9Mo_6O_{40}$ . Our refinement also suggests that Mo atoms enter the  $M1$  sites preferentially over the  $M2$  sites. The degree of ordering among the metal atoms is still very low despite the lengthy thermal annealing. A model with anisotropic temperature factors for  $M1$  and  $O5$  suggested highly anisotropic vibrations for them (space group  $C2$ ), indicative of static disorder present in the crystals. The change in  $R_{wp}$  (to 8.28%) was, however, slight. Although neutron diffraction studies are more sensitive to oxy-

FIG. 1. Upper trace: Observed (circle) and calculated (line) profile intensities for  $V_9Mo_6O_{40}$ . Lower trace: Difference profile. Vertical markers denote positions of Bragg reflections.

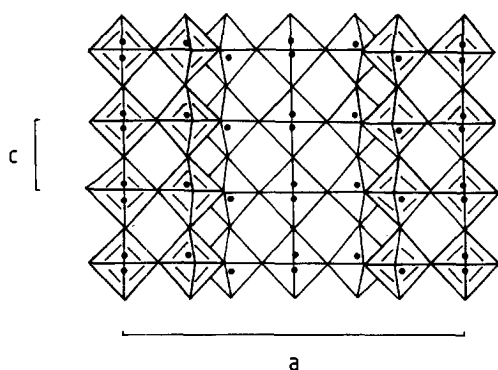


FIG. 2. Structure of  $V_9Mo_6O_{40}$  viewed along the  $b$  axis. Solid circles denote metal atom sites. The ambiguities in the  $M1$  positions are indicated.

gen ordering than X-ray diffraction studies, our results show that mere thermal annealing is not enough to bring about ordering of metal atoms. The close similarity of the results with those from  $V_2MoO_8$  (11) supports the existence of a narrow homogeneity range in the system  $V_{2-x}Mo_{1+x}O_8$  with the stoichiometry  $M_3O_8$  ( $M = V$  and  $Mo$ ); the charge neutrality is maintained by self-reduction of the metal species.

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