

Ordered Phases in the Monoxide Region of the Vanadium-Oxygen System

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The monoxide region of the V—O system is known to possess a wide range of non-stoichiometry. At high temperatures, the defect NaCl type structure VO_x extends from $x=0.8$ to $x=1.27$.¹⁻³ Below 800°C Westman and Nordmark³ reported a tetragonal phase with the homogeneity range $x=1.23-1.27$. The lattice parameters were given as $a=16.613 \text{ \AA}$, $c=16.497 \text{ \AA}$,⁴ the structure was suggested to represent an ordered arrangement of metal vacancies in a slightly deformed NaCl-type lattice, and referred to the ideal composition $\text{V}_{204}\text{O}_{256}(\text{VO}_{1.25})$.

The present note reports of a combined selected area electron diffraction and X-ray powder diffraction study of superstructures in the vanadium monoxide region: *viz.* the structure of the phase $\text{V}_{58}\text{O}_{64}$ as well as evidence for the existence of another phase of the approximate composition $\text{VO}_{1.17}$.

Experimental. Vanadium metal (Koch-Light, 99.5 %) and V_2O_5 obtained by hydrogen reduction of V_2O_5 (Johnson, Matthey & Co., spectrographic) were weighed out and arc melted together in an argon atmosphere to produce specimens of desired compositions. The samples, resting on a water-cooled copper base, were rapidly cooled to room temperature. Some of the samples were heat treated in vacuum at $790 \pm 10^\circ\text{C}$ for a period of 3 weeks and some at 1100°C for 3 days followed by further heat treatment at 800°C for 5 days and 600°C for 11 days.

Specimens for examination in the electron microscope were prepared by metallographic polishing to approximately 0.5 mm thickness, followed by electropolishing at a voltage of 13 V in an electrolyte containing 10 % perchloric acid and 90 % methanol and a final etching in slightly diluted nitric acid. Selected area diffraction patterns and electron micrographs were taken in a Philips E M 300 equipped with a goniometer stage; X-ray powder photographs were taken with a Guinier camera using $\text{CuK}\alpha$ radiation.

The tetragonal phase $\text{V}_{58}\text{O}_{64}$. Specimens with nominal composition in the range $\text{VO}_{1.20}-\text{VO}_{1.30}$ produced electron diffraction patterns which could be indexed on basis of a tetragonal unit cell with dimensions $a \approx 2\sqrt{2}a_c$, $c \approx 2a_c$ where a_c is the lattice constant of cubic VO_x . The electron micrographs revealed a domain structure with the tetragonal c -axis alternating between the three cube edge directions of the original cubic grain. The domain size was quite small so that all three orientations contributed to the selected area diffraction patterns. The indexing of the superimposed patterns from the three orientations were checked by dark field micrographs.

The lattice constants $a=11.72 \text{ \AA}$ and $c=8.245 \text{ \AA}$ were obtained from Guinier photographs. These may be compared by the values $a_{\text{WN}}/\sqrt{2}=11.747 \text{ \AA}$ and $c_{\text{WN}}/2=8.248 \text{ \AA}$ from Westman and Nordmark's investigation.

The space group $I4_1/amd$ could be unequivocally determined from the observed extinctions in the single crystal patterns; *viz.*

$$\begin{aligned} hkl &: h+k+l=2n \\ hk0 &: h, (k) \neq 2n \\ hhl &: (l=2n), 2h+l \neq 4n \end{aligned}$$

The present unit cell is 1/4 of the one given by Westman and Nordmark.³ However, since the space group includes no positions with multiplicity less than four, their composition, $\text{V}_{204}\text{O}_{256}$ or $\text{V}_{1.25}\text{O}$, cannot be retained. The ideal composition was thence taken to be $\text{V}_{58}\text{O}_{64}$ *i.e.* $\text{VO}_{1.13}$.

The structure determination was based on the space group obtained by electron diffraction and the intensities of 14 reflecting planes as determined from photometer traces of the X-ray Guinier photographs. In the space group $I4_1/amd$ the octahedral sites of the NaCl-type lattice must be 16- or 32-fold thus leaving at least four metal atoms to be placed at other sites in a fully ordered structure. Moreover, the negative peaks in a partial Patterson synthesis based on the superlattice reflections, notably near $(1/8, 0, 1/8)$, indicated vacant octahedral cation sites to be arranged around interstitial metal atoms at tetrahedral sites as in FeO (Koch and Cohen⁵). With four such interstitial atoms good agreement with observed intensities could be obtained when using the following parameters:

4 V in 4 <i>a</i>		
16 V in 16 <i>h</i>	$x=1/8, z=1/4$	
16 V in 16 <i>f</i>	$x=1/8,$	
16 V in 16 <i>f</i>	$x=5/8,$	
16 O in 16 <i>h</i>	$x=1/8, z=0$	
16 O in 16 <i>h</i>	$x=1/8, z=1/2$	
32 O in 32 <i>i</i>	$x=1/8, y=0, z=1/4$	

The *R*-factor was found to be 0.08.

This arrangement differs from the NaCl-type structure by four interstitial vanadium atoms in 4 *a* and metal vacancies in 16 *h* with $x=1/8, z=3/4$. The structure is shown in Fig. 1.

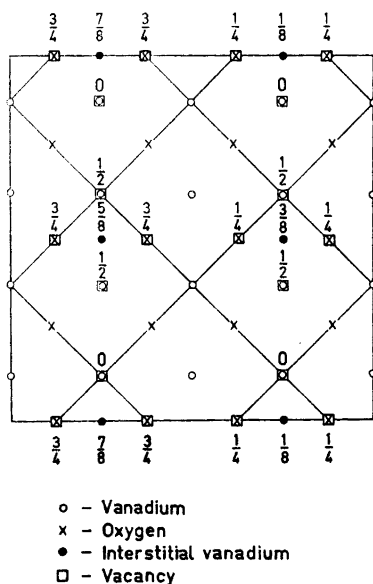


Fig. 1. The defect structure of $V_{52}O_{64}$ projected on the (001) plane. The heights are in terms of the cell unit.

The structure can be described as an ordered arrangement of groups consisting of one interstitial vanadium atom surrounded by a tetrahedron of vacancies, with four such groups in the unit cell.

No significant improvement in the *R*-factor could be obtained on distributing the interstitial vanadium atom between the tetrahedral position and the surrounding vacancies. A least square refinement of the coordinates did not lead to any significant shift from the ideal positions.

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$VO_{1.17}$. At a lower oxygen content, $x=1.16-1.20$, another tetragonal phase was found when using the second heat treatment. The lattice parameters $a=26.08 \text{ \AA}$ and $c=8.30 \text{ \AA}$ were obtained from X-ray powder photographs. From the electron diffraction pattern, the axes could be referred to the cubic unit cell as

$$a \approx 6 a_c + 2 b_c, c \approx 2 c_c$$

The space group was concluded to be $I4_1/a$ from the observed extinctions.

$$hkl: h+k+l \neq 2n, hk0: h, (k) \neq 2n$$

The last set of extinctions belonging to this space group, $00l: l \neq 4n$, is difficult to observe due to extensive twinning and multiple scattering. The electron micrographs revealed a morphology similar to the $V_{52}O_{64}$ phase, but to each orientation of the tetragonal axis there were two patterns symmetric about the (110) cubic planes, each belonging to half the crystals.

The electron diffraction pattern from this phase consists of strong fundamental reflections corresponding to the NaCl-type lattice; moderate superstructure reflections very similar to those from $V_{52}O_{64}$ and weak superlattice spots; see Fig. 2. Whether this superstructure is connected with an arrangement of metal vacancies and interstitials more complicated than in $V_{52}O_{64}$ or an ordered arrangement of oxygen vacancies (about 8%, according

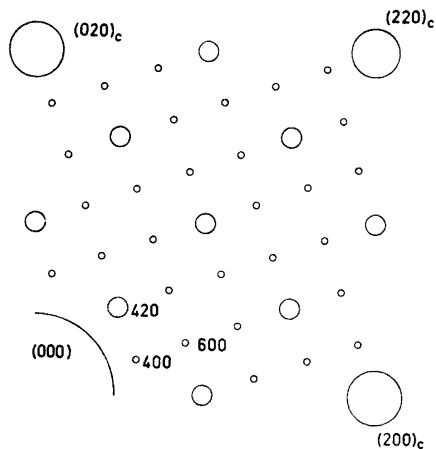


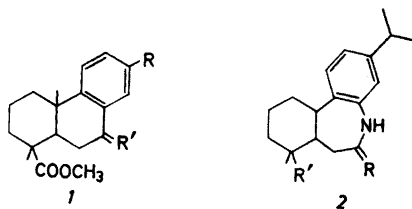
Fig. 2. One quadrant of the (001) plane of the reciprocal lattice of $VO_{1.17}$.

to Westman and Nordmark³) or both cannot be decided at the present stage.

Samples quenched from temperatures 800°C–400°C in the composition range $x = 0.90$ to 1.05 show strong diffuse scattering; two types of pattern have been noted.

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$C_{20}H_{22}NO_2$, was formed, the spectral data of which indicated structure 3 ($R=H$, $R'=COOCH_3$). This base exhibited a characteristic colour reaction with $SbCl_5$.



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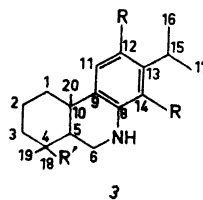
The Beckmann Rearrangement of the Oxime of 7-Ketodehydroabietate. A Side Reaction

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Dedicated to Professor K. Mothes
on his 70th birthday

Controlled oxidation of methyl dehydroabietate with chromic acid¹ gave methyl 7-ketodehydroabietate (**1**, $R=ipr$, $R'=O$) in about 75% yield. Prolonged oxidation yielded increasing amounts of the diketone **1** ($R=COCH_3$, $R'=O$). When subjected to Beckmann rearrangement (polyphosphoric acid) the oxime of ketone **1** ($R=ipr$, $R'=O$) furnished the expected lactam (**2**, $R=O$, $R'=COOCH_3$), $C_{21}H_{22}NO_2$. In addition, a weak base,



The unexpected formation of this base indicates that, in studies of Beckmann rearrangement, it may sometimes be worth-while looking not only for the normal amides but also for basic reaction products.

Experimental. Methyl dehydroabietate (10 g) in acetic acid (5.5 g) was added dropwise at 50° with stirring to chromic acid (5 g) in 75% acetic acid (15 g). After 10 h at 20° an equal amount of chromic acid solution was added and the mixture heated to 90–100°. At intervals samples were examined by gas chromatography. The heating was continued until almost all the methyl dehydroabietate had disappeared (about 3 h). The reaction products were isolated and separated on silica gel. Light petroleum:benzene (4:1) eluted the unchanged starting material and the methyl 7-ketodehydroabietate was obtained from the benzene:ether (9:1) fraction as an oil which slowly crystallized. Recrystallization from light petroleum gave crystals melting at 66–67.5° (Lit.¹ m.p. 67–68°), yield 75%. Pure ether eluted the diketone **1** ($R=COCH_3$, $R'=O$), m.p. 145–145.5°, $[\alpha]_D$ 29.3° ($CHCl_3$, $c=1.6$). Lit.¹ m.p. 144–145°, $[\alpha]_D$ 30.8° ($CHCl_3$).

The oxime of methyl 7-ketodehydroabietate was prepared in the usual way and purified by chromatography on silica (benzene:ether, 9:1). From isooctane crystals were obtained, melting at 127.5–129°, $[\alpha]_D$ –49.3° ($CHCl_3$, $c=0.9$).