One- and Two-dimensional Crystallographic Shear in Two Wolfram Vanadium Oxides of M_2O_5 Stoichiometry

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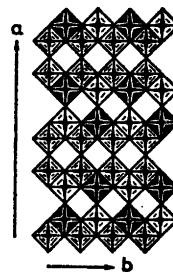

Fig. 1. The ordered structure of monoclinic $(W_{0.375}V_{0.625})_2O_5$ [$=WV(W_{0.25}V_{0.75})_2O_{10}$]. The octahedra containing (W), $(W_{0.25}V_{0.75})$ and (V) are indicated by different degrees of shading, decreasing in the above sequence.

The existence of two intermediate phases in the $W-V-O$ system was reported by Freundlich a few years ago.[1] The formula $WV_2O \sim _{7.5}$ ($=W_{0.33}V_{0.67}O_{2.5}$) was assigned to one of these which was found to be stable below 800°C and to have a *tetragonal* unit cell and the space group symmetry $I4/mmm$. The other phase, forming at higher temperatures, was assumed to have a homogeneity range, indicated in the formula $WV_2O_{6.9-7.1}$ ($=W_{0.33}V_{0.67}O_{2.30-2.37}$), and a *monoclinic* structure with space group $C2/m$.

The crystal structures of these two phases have been determined by the present authors and are briefly reported below.

Samples were prepared by heating mixtures of vanadium and wolfram oxides in evacuated, sealed platinum or silica tubes. The powder patterns of the products indicated a tetragonal phase which was obtained pure in samples of compositions close to that given by Freundlich. The monoclinic compound, however, was formed as a single phase at a composition close to $W_{0.375}V_{0.625}O_{2.5}$ ($=W_3V_5O_{20}$) and this formula was also supported by the measured density ($\varrho_{obs}=5.18$, $\varrho_{calc}=5.21$ g·cm^{-3} and by the structure analysis.

The monoclinic phase. The Weissenberg photographs of crystals of this phase revealed a doubling of the a and b axes reported by Freundlich and the following cell dimensions were obtained: $a=24.410$, $b=7.446$, $c=3.951$ Å, $\beta=91.03°$. All reflections on the odd layer lines $h1l$ and $h3l$ were diffuse, however; being considerably drawn out along a^* which indicates frequent mistakes in the periodicity in the a direction.

The analysis of the ordered structure (final $R=0.073$) showed that it is closely similar to that of $(Mo_{0.3}V_{0.7})_2O_5$[2] but with partial ordering of the W and V atoms which results in a superstructure. It can thus be described in terms of MO_6 octa-

hedra coupled together as in V_2O_5 and, accordingly, be considered formally as a structure with one-dimensional shear in a basic ReO_3-type structure.[3,4]

The structure is visualized in an idealized way in Fig. 1. It is composed of zig-zag strings of octahedra sharing edges, and these strings are coupled with identical strings along the line of sight to form layers. The octahedra on one side of these double-layers contain $(W_{0.25}V_{0.75})$ in statistical distribution, while those on the other side are filled alternately with W and V in an ordered way. The layers are stacked on top of each other with the apical oxygen corners in common and with an orientation such that "mixed" octahedra of two successive layers are paired together and so that a W octahedron is connected to an V octahedron in the neighbouring layer and *vice versa*. This stacking mode gives rise to the normal sequence of alternating twofold rotation and screw axes of space group $C2/m$.

The disorder can be explained by assuming two types of mistakes in the stacking sequence, namely (a) two successive layers are related by a screw axis instead of a rotation axis or conversely, or (b) two layers are related by a translation instead of one of the two types of symmetry axes.

The tetragonal phase. The unit cell dimensions calculated from the powder patterns were $a=19.506$, and $c=3.704$ Å, in close agreement with Freundlich's values. The observed density was $\varrho_{obs}=5.13$ g·cm^{-3}; $\varrho_{calc}=5.18$ g·cm^{-3} for $(W_{0.35}$
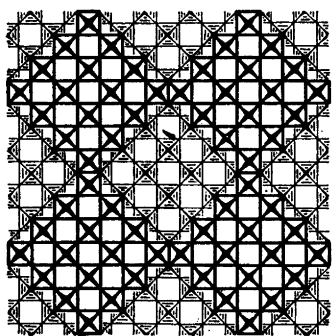
Fig. 2. The idealized structure of tetragonal $(W_{0.35}V_{0.65})_2O_5$.

$V_{0.65})_2O_5$ with $Z=16$. The space group symmetry $I4/mmm$ was confirmed by inspection of Weissenberg photographs and the structure was solved by means of Patterson syntheses. The subsequent least squares refinement based on diffractometer data resulted in a final R-value of 0.056.

The idealized structure is shown in Fig. 2. It is composed of MO_6 octahedra at two levels; $M=(W,V)$ with different W/V ratios at the three non-equivalent metal positions. 4×4 octahedra at the same level share corners and form, together with identical polyhedra above and below, a block of ReO_3-type infinite along c. Such blocks are mutually connected by component octahedra having edges in common. Two equivalent sets of mutually perpendicular shear planes are thus formed and the structure can formally be derived from the ReO_3-type structure by displacement of $(4 \times 4 \times \infty)$-blocks the vectors $(\frac{1}{2}a+\frac{1}{2}c)$ and $(\frac{1}{2}b+\frac{1}{2}c)$ relative to each other along the two sets of shear planes, respectively; a, b, and c being the edges of the ReO_3-type subcell. If a shear mechanism operates in a basic ReO_3-type structure in two stages, first along one set of shear planes and thereafter along the other, the present structure type is formed.

A large number of "block structures" have been described by Roth and Wadsley.[5] These and other multiple-shear structures have been systematized by Andersson.[4,6] Although the present structure is obviously of this type, it does not fit into the classification, but forms the first known member of a new group of structures with a very simple shear mechanism. Further

members of this group can be obtained by variation of the block-size according to the principles of homologous series.[3] It may be noticed that there is a relationship between this structure and that of N-Nb_2O_5 which is also composed of 4×4 blocks [7] but with a different shear mechanism.

Full details of the investigations reported above will shortly be published elsewhere.

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On the Structure of the Dichloroiodide Ion

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The crystal structure of triethylenediammonium *bis*-dichloroiodide,

$$\left[\begin{array}{c} NH \\ CH_2 \;\; CH_2 \;\; CH_2 \\ CH_2 \;\; CH_2 \;\; CH_2 \\ NH \end{array}\right]^{2+} \cdot \; 2(Cl-I-Cl)^-$$