

## An Electron Microscope Study of Tungsten Oxides in the Composition Range $WO_{2.90}$ - $WO_{2.72}$

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The structures of tungsten oxides occurring in the composition range  $WO_{2.90}$ - $WO_{2.72}$  have been studied by transmission electron microscopy. In the oxygen-rich part of the phase range  $W_nO_{3n-2}$  CS phases exist. The lowest value of  $n$  found for extensive areas of ordered material was 16. At the oxygen-poor end of the phase range,  $W_{18}O_{49}$  exists. No evidence was found to indicate that this phase has an appreciable composition range. Between the  $W_nO_{3n-2}$  oxides and  $W_{18}O_{49}$  a previously unreported oxide was found. Its structure has been partly elucidated by high-resolution electron microscopy and it has been shown to bear more resemblance to a tunnel structure than to a CS phase.

### Introduction

Within the oxygen-rich region of the binary tungsten-oxygen system, four different structural types have been reported. These are  $WO_3$ , which has a slightly distorted  $ReO_3$  ( $DO_9$ ) type of structure (1), consisting of an infinite array of corner sharing  $WO_6$  octahedra, two homologous series of oxides with formulas  $W_nO_{3n-1}$  and  $W_nO_{3n-2}$  derived from the  $WO_3$  structure by crystallographic shear (CS) upon {102} and {103} planes, respectively (2-4), and a tunnel compound,  $W_{18}O_{49}$  (5). All of these phases have a clearly recognizable structural skeleton of  $WO_3$ , linked by units of edge sharing octahedra in the CS phases and by more complex groupings of octahedra which place tungsten atoms in pentagonal tunnels in  $W_{18}O_{49}$ . The structures of  $W_{20}O_{58}$ , containing {103} CS planes and  $W_{18}O_{49}$  are shown in Fig. 1.

Electron microscope studies have done much to clarify the structural relationships found in the composition range  $WO_3$  to  $WO_{2.88}$  (6-11). For samples prepared at temperatures of the order of 1300°K the

stoichiometry of the oxide has been shown to be a function of the number and spacing of the CS planes present in the  $WO_3$ -like parent matrix. At the oxygen-rich end {102} CS planes are found. They are invariably disordered and frequently occur in small isolated groups in the parent structure. At greater degrees of reduction quasi-ordered  $W_nO_{3n-1}$  oxides form. The lowest value of  $n$  found for fairly well-ordered samples seems to be 12, although in disordered materials individual pairs or small groups of CS planes may be closer together than in  $W_{12}O_{35}$  and represent lamellae of lower oxides one or more unit cells wide in which a value of  $n$  less than 12 is applicable. At compositions below about  $WO_{2.92}$ , {103} CS planes become dominant and crystals are members of the homologous series  $W_nO_{3n-2}$  when ordered. The upper limit found for well-ordered members of this series is approximately  $W_{26}O_{76}$  although wider spacings have been observed. Isolated {103} CS planes existing in  $WO_3$  have not been reported in the literature so far. The lower limit of the series is uncertain, but may be close to  $W_{13}O_{37}$ . As in the case of the {102} CS phases, the CS

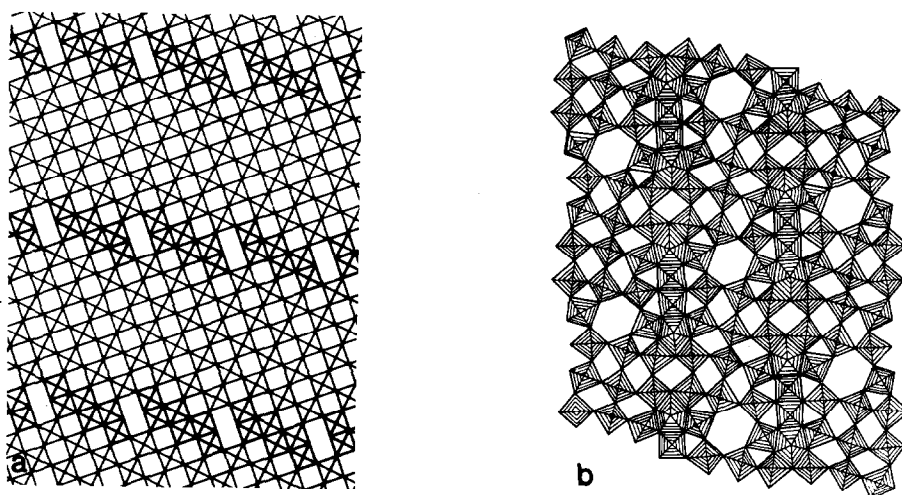


FIG. 1. (a) The idealized structure of  $W_{20}O_{58}$  projected along  $[010]$ . (b) The real structure of  $W_{18}O_{49}$  projected along  $[010]$ . Both structures contain extensive volumes of corner-shared  $WO_6$  octahedra represented as ideal (unshaded) squares in (a) and as distorted (shaded) squares in (b) in the projections used.

planes are more usually disordered than ordered, and a variety of spacings can be observed in most fragments.

Thus, within the composition range  $WO_3$  to approximately  $WO_{2.88}$  a crystal can have any particular composition by adjusting the number and type of *CS* planes present. Therefore, the *CS* planes can be regarded as chemical defects whose presence in a crystal provides an extremely flexible way of accommodating different metal to oxygen ratios.

The severe disorder present in the majority of these *CS* phases has been the principal reason for the very few single-crystal X-ray studies of these compounds that are to be found in the literature (2-4). In addition the large unit cells possessed by the *CS* phases and the fact that they are all structurally similar has led to difficulties in interpreting X-ray powder data of mixtures unequivocally. However, at present, X-ray powder studies provide the only experimental data available to indicate which structures are occurring in the composition interval between  $WO_{2.90}$  and  $WO_{2.72}$  ( $W_{18}O_{49}$ ). These data have been interpreted as indicating that  $W_nO_{3n-2}$  oxides are found at the oxygen-rich end of the range

and  $W_{18}O_{49}$  is found at the lower end. Between the two extremes, these two structural types are considered to coexist, but the X-ray data have been unable to yield a value for the lowest member of the  $W_nO_{3n-2}$  series to be found due to the disordered nature of the crystals obtained. The X-ray evidence, however, has indicated positively that the oxide  $W_{18}O_{49}$  is strictly stoichiometric, with no observable composition range (5, 12) in accord with the most recent thermodynamic studies (13).

As electron microscopy is not so seriously hampered by severe structural disorder of the sort commonly found in these oxides, a study of this region of the tungsten-oxygen system was undertaken to clarify the structures existing in samples prepared at about 1300°K. This communication describes the results obtained. Besides the  $W_nO_{3n-2}$  and  $W_{18}O_{49}$  oxides, which were readily identified by reference to earlier work (3-11), a new structure was also found, with an estimated composition close to  $WO_{2.82}$ . Some suggestions as to the structure of this new compound are made, based on high-resolution electron micrographs. The way in which stoichiometric

variation is accommodated across the composition range  $\text{WO}_{2.90}$  to  $\text{WO}_{2.72}$  is also clarified.

### Experimental

Samples with an overall composition between  $\text{WO}_{2.90}$  and  $\text{WO}_{2.72}$  were prepared by heating tungsten trioxide with tungsten metal powder or turnings from the same source in sealed silica ampoules. The tungsten trioxide was in the form of a fine powder or small crystallites. All chemicals were of high purity, and were supplied by Johnson Matthey Ltd. (Specpure grade) or Koch-Light Laboratories. Heating times of from several days to 3 months at temperatures in the range 1173 to 1373°K were employed. The ampoules were usually evacuated, but transporting and mineralizing agents were sometimes used in attempts to promote crystal growth.

After reaction, the materials present in the tubes were examined optically. Where possible, crystals of differing habit or appearance were separated and examined further by electron microscopy. In some cases, a manual separation was not possible and electron microscope specimens were prepared from average material. Mean compositions of the samples were determined by oxidation to  $\text{WO}_{3.0}$  using a Sartorius model 4102 microbalance.

For high-resolution electron microscopy, samples were crushed in an agate mortar and dispersed in *n*-butanol. Drops of this suspension were dried on perforated carbon films. Crystal fragments that projected over holes in the support film were examined using a JEM 100B electron microscope under the operating conditions specified by Iijima (14) and Allpress and Sanders (15) in order to obtain images that could be interpreted in terms of the projected charge density of the crystal.

### Results

At the higher end of the composition range, samples were made up of very dark blue-black crystals with a needle-like habit. Electron microscope examination showed that they

consisted of  $\text{W}_n\text{O}_{3n-2}$  oxides containing quasi-ordered {103} CS planes. The lowest value of *n* found in fairly well-ordered crystals was 16, corresponding to an oxide of composition  $\text{W}_{16}\text{O}_{46}$ , viz.  $\text{WO}_{2.875}$ , although isolated lamellae of narrower spacings were also seen. However, all samples were inhomogeneous, and a wide variety of *n* values was found in each sample, with 18 predominating. The material, which was very similar to that reported by Allpress and Gadó (5), is illustrated in Fig. 2 and can be directly compared with the structure shown in Fig. 1.

At the lower end of the composition range, samples were of a mauve color and consisted of dense compacts of  $\text{W}_{18}\text{O}_{49}$  crystals, of a whisker or needle habit. Electron microscope examination showed that most crystal fragments were perfect, with twin boundaries being the only common fault observed. The nature of these crystals did not change when

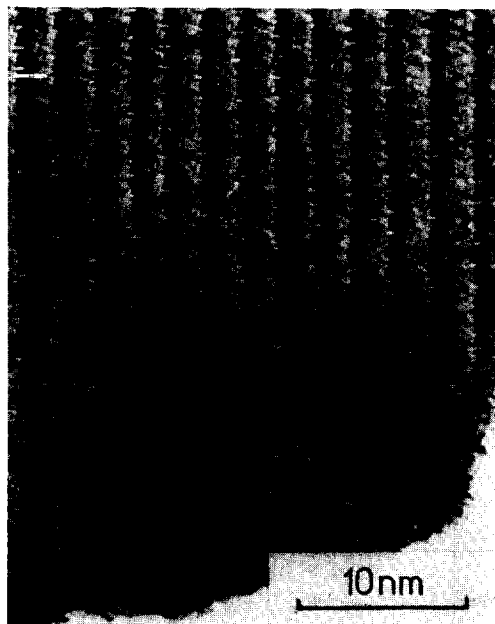


FIG. 2. High-resolution image of {103} CS planes in a reduced tungsten oxide. The CS plane contrast consists of dark blocks (equivalent to the groups of six edge-shared octahedra in Fig. 1a) separated by pale strips (equivalent to the small empty tunnels shown in Fig. 1a). The spacing of the planes is variable, but close to that in an oxide of formula  $\text{W}_{18}\text{O}_{52}$ .

they were obtained from samples of higher or lower gross composition, and it would appear that the material is strictly stoichiometric, in accordance with other findings (5, 12, 13). The electron microscope contrast is in good agreement with the structure determined by Magnéli (5), as can be seen by comparing Fig. 1 with Fig. 3, which shows a diffraction pattern and medium magnification image of part of a perfect flake of  $W_{18}O_{49}$ .

Between the  $W_nO_{3n-2}$  oxides and  $W_{18}O_{49}$ , the color of the sample changed progressively, passing through an ultramarine blue at compositions close to  $WO_{2.80}$ . In this middle range of compositions, the product invariably took the form of a hard pellet, and despite many attempts well-faceted crystals could not be grown, even when chemical transporting agents were used.

Electron microscopy revealed that fragments from these samples contained three different structural types, the  $W_nO_{3n-2}$  phases,  $W_{18}O_{49}$ , and what appeared to be a previously unreported structure. The proportions of the phases present in each sample varied considerably with bulk composition and with heating time; the new structure was most commonly found in samples heated for the longest periods of time.

After initial experiments had revealed the presence of this new material, attempts were

made to prepare it pure and in the form of single crystals. Mineralizers such as HCl and transporting agents such as  $Cl_2$  were employed for this purpose, and both the ampoule dimensions and the preparation temperatures were varied. Unfortunately, none of these attempts was successful in producing a monophasic product and because of this reliable compositional or X-ray data could not be obtained. The gross compositions of the many samples prepared in this phase range, however, did indicate that the composition of the new material was close to  $WO_{2.82}$ .

In the electron microscope, crystal fragments which were of this new type were always severely disordered, as Fig. 4 shows. Adjacent grains were often tilted with respect to each other, as could be seen from the fact that several curved arcs of spots were usually found on selected area diffraction patterns of apparently single fragments. Occasionally, in samples with gross compositions close to  $WO_{2.86}$ , this new phase was joined coherently to grains containing {103} CS planes. However, intergrowth of this new structure with  $W_{18}O_{49}$ , or intergrowths between  $W_{18}O_{49}$  and the  $W_nO_{3n-2}$  oxides were not observed.

Selected area diffraction patterns from the new structure were usually twinned due to the disordered nature of the crystal fragments found, but occasionally grains were large

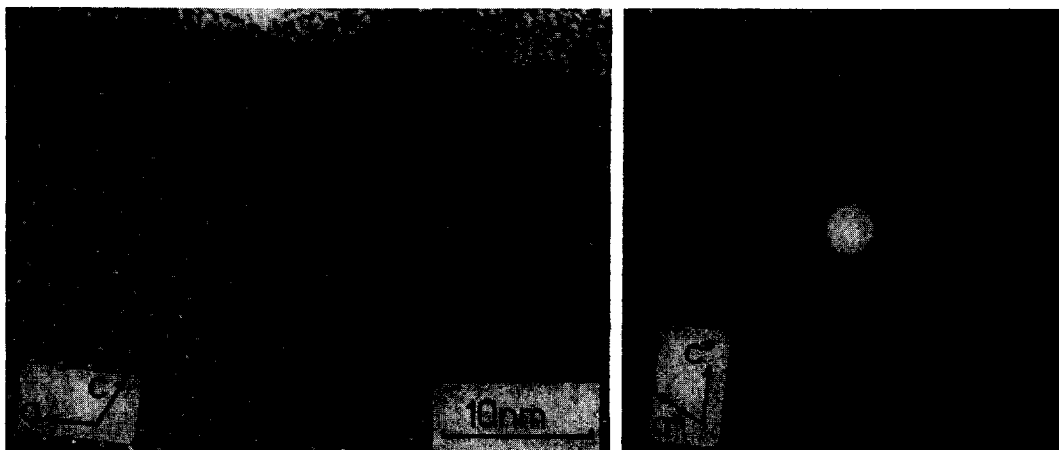


FIG. 3. (a) High-resolution image of  $W_{18}O_{49}$ , projected along [010] and (b) corresponding diffraction pattern, correctly oriented with the micrograph. The hexagonal tunnels in the structure are clearly visible as white spots on the micrograph.



FIG. 4. (a) Medium magnification image of the  $\text{WO}_{2.82}$  oxide showing the typically disordered nature of the fragments.

enough to yield untwinned patterns if the smallest selected area aperture was used. Figure 5 shows both twinned and untwinned diffraction patterns. From these it was clear that the unit cell was large in two dimensions and that the stronger reflections fell on the positions expected for a  $\text{WO}_3$  type of unit cell. Thus, one could conclude that the phase must

be related to the  $\text{WO}_3$  structure and that it probably contained a significant number of corner-sharing  $\text{WO}_6$  octahedra. Furthermore, it is evident from the sharpness of the  $\text{WO}_3$  subcell spots in Fig. 5a that the twinning does not affect the underlying  $\text{WO}_3$ -like substructure and indicates that the basic  $\text{WO}_3$ -like network passes coherently and with little

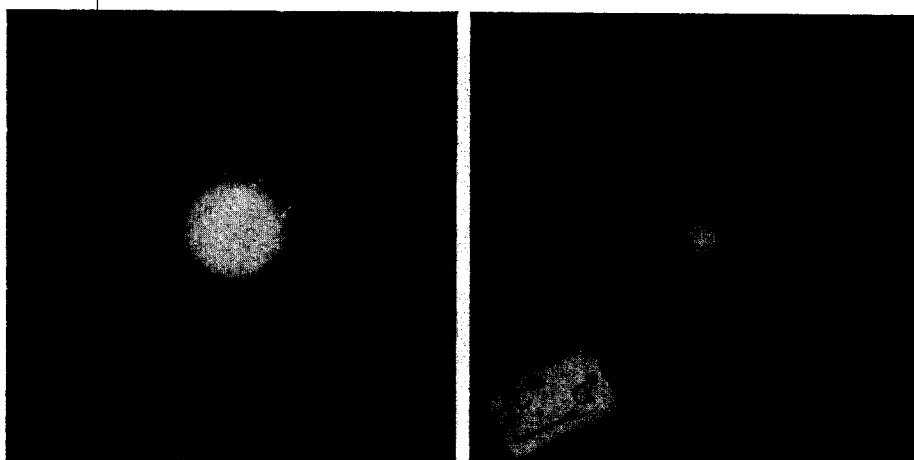


FIG. 5. Diffraction patterns of the  $\text{WO}_{2.82}$  oxide. (a) From a fragment of the sort shown in Fig. 4, revealing substantial twinning; (b) from an untwinned fragment.

change from one twin domain to another. Tilting of such crystal flakes also indicated that the other crystal axis was fairly short.

By analogy with the crystal chemistry of the other tungsten oxides in this composition range, it was assumed that this axis was normal

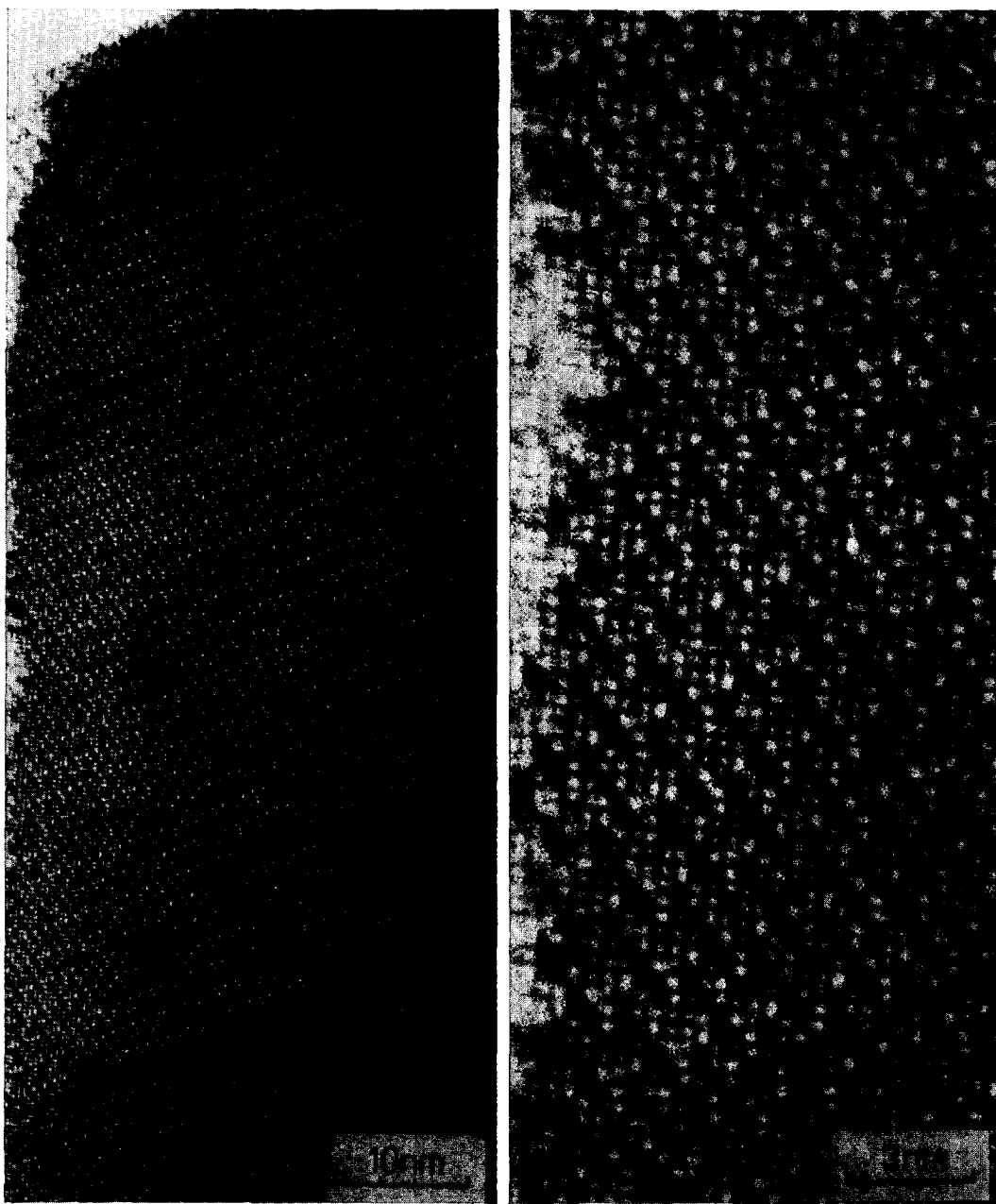


FIG. 6. (a) High-resolution image of a well-ordered flake of the tungsten oxide phase shown in Fig. 4. A small twinned region, and a wider strip of "WO<sub>3</sub>" structure are seen. (b) Enlarged image of a portion of (a) revealing the substructure clearly. The unit cell is outlined.

to the reciprocal lattice section shown in Fig. 5, and about 0.38 nm long. An approximate unit cell could then be derived. The cell chosen is monoclinic and has dimensions:  $a = 1.93$  nm,  $b = 0.38$  nm,  $c = 1.71$  nm, and  $\beta = 103.5^\circ$ .

To obtain information on the structure of this material, high-resolution electron micrographs were obtained. Figure 6 shows the contrast of a thin flake of material when the  $b$  axis was aligned parallel to the electron beam and approximately 100 beams were allowed to contribute to the image. From such images it is at once clear that the material does not contain planar  $CS$  faults of the type found in the  $W_nO_{3n-1}$  or  $W_nO_{3n-2}$  oxides, illustrated in Figs. 1 and 2. Moreover, the phase can be seen to contain extensive areas of  $WO_3$ -like corner-sharing octahedra but no extensive array of large hexagonal tunnels as in  $W_{18}O_{49}$ . The structure is therefore of a new type previously undescribed in this system.

Models certainly can be derived for the structure based upon the contrast in Fig. 6, assuming that the projected charge density of the crystal structure is related to the image density shown (15). However, both theoretical calculations (15, 16) and experimentally obtained images (17, 18) have shown that this naive approximation is only valid under an extremely narrow range of operationable variables, which include the thickness and orientation of the sample and the departure from exact focus of the electron microscope. Consideration of these reports makes it clear that quite erroneous models could be derived and that the only certain way to confirm plausible structures is to compute the expected high-resolution image theoretically and compare it with the experimentally obtained images. This task is now being undertaken in collaboration with the University of Stockholm and the results will appear in due course.

## Discussion

In agreement with earlier reports, all crystals of the  $W_nO_{3n-2}$  oxides examined contained a variety of  $CS$  plane spacings with some fragments being severely disordered

while others were almost regular in spacing. The present studies indicated that the lower limit of fairly well-ordered  $W_nO_{3n-2}$  oxides occurring in these preparations corresponded to the oxide  $W_{16}O_{46}$ . It can be concluded, therefore, that at the preparation temperatures used, the unfavorable energy terms involved in  $CS$  plane ordering are becoming dominant at  $CS$  plane spacings of approximately 1.9 nm. However, closer spacings are observed at isolated places in crystal flakes of these oxides and are frequently produced when oxides with higher  $n$  values are heated in the electron beam (9, 19). This suggests that the distribution of  $CS$  plane spacings in these oxides may well be dependent upon the temperature of the preparation and concurs with the findings of Bursill and Hyde (11). Therefore, some variation in the value of the lowest ordered homolog found in any particular experiment is to be expected and a careful series of studies over a wider range of temperatures is needed to resolve this point.

The disorder always present in these  $W_nO_{3n-2}$  crystal flakes was not paralleled in any way by the  $W_{18}O_{49}$  crystals. These latter were usually very well ordered and did not show any noticeable differences when they were taken from preparations with compositions either above or below  $WO_{2.72}$ . From a geometrical point of view this is surprising, as the rows of filled pentagonal tunnels and empty hexagonal tunnels in this structure are separated by continuous strips of  $WO_3$ -like structure, and many different homologs derived from  $W_{18}O_{49}$  could be conceived merely by altering the width of this strip. That such a process appears not to occur, at least in preparations at 1173 to 1300°K, reflects the stability of the particular arrangements found in  $W_{18}O_{49}$  which may well be connected with the rather considerable distortions in the  $WO_6$  octahedra present and which are ignored in idealized models.

The most interesting result was the discovery of the structure shown in Figs. 4-6. Although the detailed structure is, as yet, uncertain, a comparison of the electron diffraction patterns and high-resolution electron micrographs of this phase with corresponding data for the other tungsten oxides

reveals that the structure is quite different from those reported previously. Moreover, it appears to be related more closely to the tunnel compounds and  $W_{18}O_{49}$  than to the *CS* phases.

Unlike  $W_{18}O_{49}$ , this new material is very difficult to prepare and all attempts to make it in the form of single crystals, or even as a monophasic polycrystalline powder for Guinier-Hägg X-ray studies have failed so far. Indeed, the fact that so much structural information has been obtained for this material can be attributed to the power of high-resolution electron microscopy when applied to the phase analysis of such disordered multicomponent mixtures. The observation that it occurs in larger proportions in samples heated for the longest times suggests that it is very slow to form and may be only slightly more stable than the neighboring  $W_nO_{3n-2}$  and  $W_{18}O_{49}$  oxide phases. Furthermore, the way in which it has been found to intergrow with the  $W_nO_{3n-2}$  oxides may imply that it forms from them by a solid-state transformation. Such a solid-state reaction mechanism would account both for the slow rate of formation of the phase and the difficulty in preparing it pure, but growth via the vapor phase, which is prevalent in these tungsten oxides at high temperatures, may well be involved to a certain extent. The present experiments do not indicate whether this is the case.

The severe disorder found in the majority of samples of the new material could also arise from solid-state transformations. In many regions, the rows of dark spots that characterize the high-resolution micrographs of the new structure are separated by wider or narrower strips of  $WO_3$ -like matrix. This is clearly revealed in Fig. 6a, where one such isolated strip is seen. Where such wider and narrower strips meet, discontinuities arise in the rows of spots, leaving substantial areas of  $WO_3$  at some junctions. The behavior of these rows of spots parallels that of *CS* planes, in fact, and in an analogous fashion, a wide range of homologous structures can be envisaged in which both the spacing between the rows of spots and their direction in the  $WO_3$  matrix are allowed variables. However, as with

$W_{18}O_{49}$  the distortions present in the real structures may be such as to favor only one arrangement of  $WO_6$  octahedra over all others.

As it stands, the disorder observed in fragments of this new structure does indicate that on a microscopic scale quite considerable composition ranges occur. As can be seen from the micrographs, particularly Fig. 4, the density of the dark spots that characterize the material often varies considerably, particularly at junctions between grains or at other discontinuities. Detailed models for such stoichiometric variation will be constructed when the exact structure of the ordered phase has been determined.

From the results presented here, one can see that the flexibility of the tungsten trioxide structure type towards accommodating changes in stoichiometry is rather greater than previously believed. In the composition range between the  $W_nO_{3n-2}$  oxides and the stoichiometric  $W_{18}O_{49}$ , a previously unreported phase occurs which appears to be structurally related to the tunnel compounds and has an approximate composition of  $WO_{2.82}$ . This material itself seems to be capable of tolerating stoichiometric variation by varying the geometrical disposition and width of the  $WO_3$  matrix slabs that act as the skeleton of the phase. Further experiments are being carried out to see if such variation is only associated with grain boundaries and similar faults in the crystal or whether, in some circumstances, homologous structures can form that will span an appreciable composition range.

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