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An Electron Microscope Study of some Nonstoichiometric Tungsten Oxides

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Large crystals of WO_3 have been reduced to a composition of approximately $WO_{2.91}$ at 3 different temperatures, 950, 1000, and 1070°C. After reduction the crystals were examined by optical microscopy and transmission electron microscopy. The crystals were faulted in a variety of ways and rarely perfectly ordered. Large crystals heated at 1070°C supported oxygen loss by formation of {103} CS planes while crystals heated at 950°C contained {102} CS planes. At 1000°C {102} and {103} CS planes coexisted. It was found that the way in which the WO_3 structure accommodated oxygen loss was a function of composition and of temperature. In all experiments, some vapour transport also took place, resulting in the growth of needle shaped crystals. These were always members of the W_nO_{3n-2} homologous series of oxides, and contained {103} CS planes, irrespective of the formation temperature.

Introduction

Since Magnéli first determined the structure of $W_{20}O_{58}$ (*1*), and showed it to consist of largely unchanged slabs of WO_3 joined along {103}[1] crystallographic shear (CS) planes, there has been considerable interest in the nature of the phases found in the WO_3 to $WO_{2.90}$ range of the binary tungsten–oxygen system. Likewise, the mode of evolution of the WO_3 structure into one containing ordered {103} CS planes has been the subject of considerable speculation. X-ray studies, using powder and single crystal methods were unable to clarify the situation, due to the severe disorder invariably found in these crystals although phases of composition $W_{24}O_{70}$ (*2*), $W_{25}O_{73}$ (*2*), $W_{40}O_{118}$ (*3*), and $W_{50}O_{148}$ (*4*) have been characterised. These are all members of the same W_nO_{3n-2} homologous series of oxides as $W_{20}O_{58}$, having ordered {103} CS planes and differing from each other merely in the separation between the CS planes, except for $W_{50}O_{148}$, which was described as having an oxygen atom in the space between the groups of 6 edge shared octahedra which characterize {103} CS planes.

The use of transmission electron microscopy has modified the picture considerably. Allpress and Gadó (*5*) studied crystals of the W_nO_{3n-2} series which had a composition close to $WO_{2.90}$. These had a needlelike habit which indicated that they had probably formed via a vapour phase intermediate step. They found considerable disorder to be present in the CS planes which were observed in these crystals. The CS plane spacings were variable and corresponded to a range of compositions from $W_{12}O_{34}$ to $W_{28}O_{82}$. Only {103} CS planes were observed. In contrast to this, Tilley (*6*) and Allpress, Tilley and Sienko (*7*) found what were essentially isolated CS planes lying on {102} planes in large slightly reduced crystals of WO_3. The estimated compositions of these crystals were between WO_3 and $WO_{2.99}$.

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[1] All indices are referred to an idealised WO_3 (ReO_3 type) lattice.

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This has led to speculation about the nature of the defect structure of reduced tungsten trioxide in the composition range $WO_{2.99}$ to $WO_{2.90}$. Analogies with the very elegant work of Bursill and Hyde (*8*) on the titanium and titanium–chromium oxides suggested that at some composition between $WO_{2.99}$ and $WO_{2.90}$, the {102} CS plane structure should give way to a set based upon {103} CS planes. There is then the likelihood that in this part of the phase diagram a continuously variable group of CS plane indices, "swinging CS planes," should be found. Bursill and Hyde (*9*) did look for this behaviour in ReO_3 based oxides but did not report on the binary tungsten–oxygen system in depth and did not find swinging CS planes in any undoped oxides.

The present study goes some way towards filling this gap in the phase diagram. The aim was to explore the nature of reduced tungsten trioxide in the composition range near to $WO_{2.91}$ using transmission electron microscopy. The earlier studies cited above and other work in these laboratories had shown that samples with composition close to $WO_{2.91}$ prepared from powders or small crystals invariably had a needlelike habit. These needles were presumed to have formed by way of an intermediate vapour species although the mechanism of this process was unknown. Structurally the evidence indicated that they were CS phases based upon {103} CS planes (*5*). While these compounds may well be the thermodynamically stable phases in the tungsten–oxygen system under the preparation conditions normally used, the possible intervention of a vapour-phase step in their formation suggested that the defect structure of tungsten trioxide crystals reduced to a similar composition might well be different. Indeed, the only other electron microscope studies on reduced tungsten trioxide crystals (*6, 7*) indicated that {102} CS planes might be preferred in such a case. In order to clarify this ambiguity large crystals of tungsten trioxide were chosen, so that after reduction some of the original matrix would be available for examination even if evaporation of the outer surfaces took place.

Some results of this study are presented here. A number of defect structures have been found, and the conditions under which {102} CS structures give way to {103} structures have been clarified. Crystals of needle habit were also formed, and their {103} CS structure verified.

Experimental

Large crystals of WO_3 or WO_{3-x} with compositions very close to stoichiometric were sealed in evacuated silica tubes with sufficient tungsten metal to give overall compositions in the range $WO_{2.92}$–$WO_{2.90}$. The crystals used in this study were from the same stock described by Berak and Sienko previously (*10*). They were chunky and all were greater than 2 mm diam. The silica tubes were heated at temperatures between 950 and 1070°C for periods of time varying from 5 to 10 days.

The products of reaction were surveyed optically and some crystals were examined further by transmission electron microscopy. For this purpose, the selected crystals or crystal pieces were crushed in an agate mortar and dispersed in *n*-butanol. The fragments so obtained were collected on carbon coated support grids and examined in a JEM 100B electron microscope operating at 100 kV, using a goniometer stage. As high resolution images were sought the techniques described by Iijima (*11*) and Allpress and Sanders (*12*) were employed. That is, only thin flakes projecting over holes in the support film were photographed and then only after the flake had been aligned so that the short crystal *b* axis was parallel to the electron beam. This allowed imaging of the (*h*0*l*) plane in projection. In the present work, conventional filaments and a primary magnification of 300,000× were used.

Results

Optical examination of the samples after heating showed a number of different products in the tubes. These could broadly be classified into three groups. Firstly, a large number of dark blue crystals with a needle-like habit were always found growing on the surface of the original large crystals of WO_3, and at other points in the sample tube far removed from the original material. Secondly, a very small number of vapour transported crystals with a chunky habit were also found. Finally, the large crystals originally put into the tubes were also still present and were recovered.

As the main interest in this study was the defect structure of reduced tungsten trioxide, these large crystals were examined in greatest detail. Their colour had changed from green to dark blue-black and did not vary greatly from the outside to the middle of the crystals indicating qualitatively that reduction had occurred throughout the bulk. The outside of the crystals were covered in a dense layer of needlelike crystals. Below this, the original crystal surface also appeared to have transformed into needles resulting in a pseudomorphic appearance. With small crystals, this pseudomorphic transformation can be complete, but in the larger crystals employed in these experiments, the central regions were not composed of needles. For the purposes of electron microscopy, pieces of these large crystals were selected for examination only if they appeared to be free of needles. Thus the results obtained from such material represents the nature of the tungsten trioxide structure after reduction rather than that of any vapour grown species.

For the sake of comparison needles from some samples were also examined electron optically. As these results were less complex than those from the large crystals, they are considered first.

Crystals with a Needle Habit

The needle fragments examined always showed {103} CS structures regardless of the preparation temperature. These were frequently faulted in a variety of ways and only rarely were they perfectly ordered. Their compositions fell in the range $W_{12}O_{34}$–$W_{28}O_{82}$ described by Allpress and Gadó (*5*). Figure 1 shows the (*h*0*l*) lattice image from a quite well ordered fragment. The diffraction pattern showed that the material was a CS phase, with composition close to $W_{18}O_{52}$, and that the CS planes were on (301). A relevant interpretation of the contrast in Fig. 1 can be made if one assumes that the darker areas correspond to regions in the crystal which contain a higher projected charge density. This interpretation is subject to a number of limitations which have been discussed at length by Iijima (*11*) and Allpress and Sanders (*12*). These authors, however, have shown that such an interpretation is valid

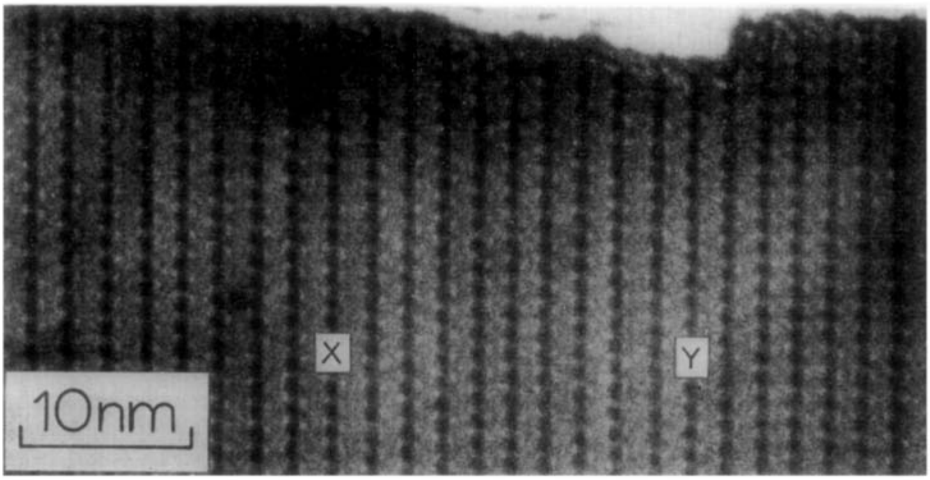

FIG. 1. Lattice image of (301) CS planes in a fragment from a needle shaped crystal. The composition of the region shown is close to $W_{18}O_{52}$. The area between the CS planes labelled X and Y is also shown in Fig. 2.

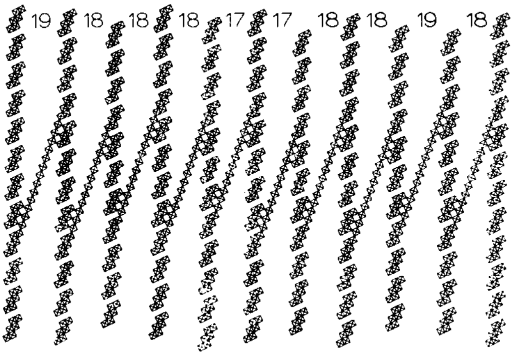

FIG. 2. Idealized representation of the structure of the area of crystal shown in Fig. 1 between the CS planes labelled X and Y. Only the octahedra within the CS plane are shown except for one row of octahedra between each CS plane which reveals the orientation of the WO_3 matrix. The numbers between each CS plane refer to the value of n in the series formula W_nO_{3n-2} which is also equal to the number of octahedra in the diagonal rows between the CS planes.

for the thin crystals and diffraction conditions employed here. Therefore, one is able to relate the darkest regions of the crystal to groups of 6 octahedra sharing edges, which is the structural motif of the {103} series of phases. Figure 2 shows an idealized representation of part of Fig. 1 in which the edge-shared (WO_6) octahedra in the CS plane are drawn and the parent WO_3 matrix lying between the CS planes has been omitted for clarity. It is seen that the spacing between the CS planes varies although the region appears to be well ordered at first sight.

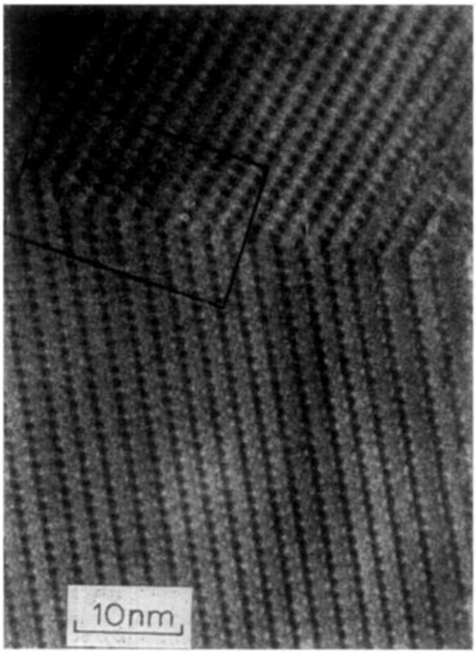

FIG. 3. Lattice image of a twinned region in the same crystal fragment as shown in Fig. 1. CS is on (301) planes in the lower region and $(\bar{3}01)$ planes in the upper part. The area within the box is shown in Fig. 4.

Twinning was the most frequently observed defect in these needle crystals. Figure 3 shows a different region of the same crystal flake as shown in Fig. 1. It contains, as well as the (301) CS planes, a set on $(\bar{3}01)$ planes in a twinned orientation with respect to the former. It is seen that the twin boundary is not along a single crystallographic direction and does not form a unique composition plane, although part of this boundary lies along (001). Such boundaries are perhaps better described as subgrain boundaries. Figure 4 shows the structure of part of the twin boundary shown in Fig. 3. Some distortion of the parent WO_6 octahedra must take place in the neighbourhood of this boundary, particularly in the region close to the CS plane which terminates. As no information about this distortion is available from the micrograph, such detail has been omitted from Fig. 4.

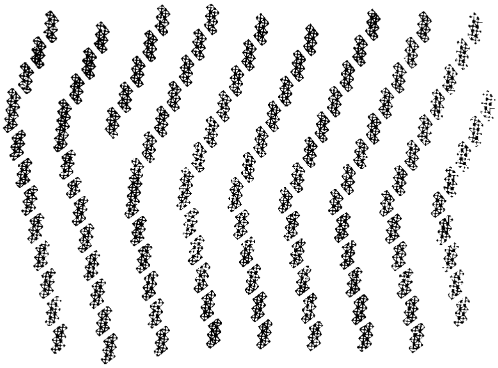

FIG. 4. Idealized representation of the structure of the area of Fig. 3 enclosed in a box showing a variety of edge-shared groups of octahedra at the twin boundary. Only the linkage of octahedra within the CS plane is shown; the WO_3 matrix being omitted for clarity.

Large WO_3 Crystals Heated at 1070°C

Analysis of fragments from the large WO_{3-x} crystals heated at 1070°C showed CS parallel to {103}. These CS planes were usually less well ordered than the corresponding needle fragments but were comparable with Figs. 1 and 3.

A disordered fragment containing (10$\bar{3}$) CS planes is shown in Fig. 5. Two features are immediately apparent, CS planes terminating at X for example, and a sequence of CS plane pairs. If one takes the wider spaced CS planes, those labelled Y, it is found that they form the basic substructure found in the diffraction pattern, in this case corresponding to $W_{23}O_{67}$. None of this set of CS planes are observed to terminate in the crystal. The ones belonging to the set X that do terminate are only rarely found in the middle of the wider set Y and more usually divide the space between these CS planes into uneven parts. There is some variation in this spacing, but in general the resulting narrow pair of CS planes correspond to lamellae of oxides close to $W_{10}O_{28}$. In addition almost all of the CS plane set X are not exactly straight and at Z, for example, a CS plane is found which is at an appreciable angle to those on either side of it. The direction that these CS planes take is most frequently towards (10$\bar{2}$). This suggests that a considerable proportion of groups of 4 edge-shared octahedra which are characteristic of {102} CS planes have intergrown with the groups of 6 edge-shared octahedra of the {103} CS planes. Such a situation allows the composition of the material to be slightly higher than if a perfect set of {103} CS planes were present.

An interpretation of the difference between these 2 sets of CS planes which is consistent with the appearance of Fig. 5 is to suppose

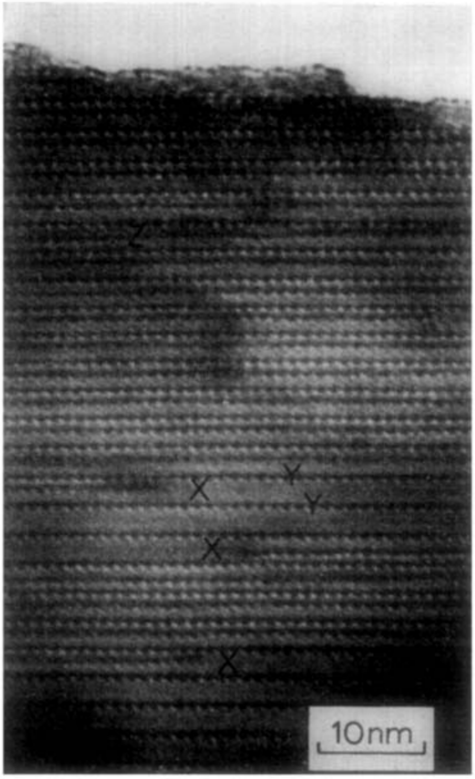

FIG. 5. Lattice image of a fragment from a large WO_3 crystal reduced at 1070°C. The CS planes are on (10$\bar{3}$). One set of CS planes, X, are observed to terminate and to wander in direction. The other set, Y, are better ordered and correspond to an oxide $W_{23}O_{67}$.

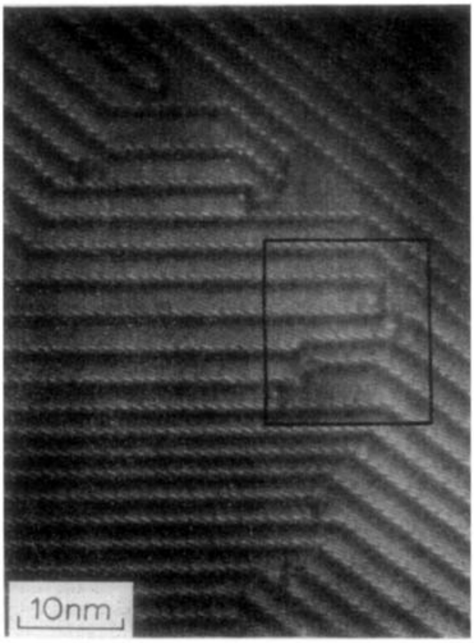

FIG. 6. Lattice image of a fragment from a large WO_3 crystal reduced at 1070°C showing twinning of the CS planes which lie on (301) planes (left) and ($\bar{3}$01) planes (right). The area enclosed in the box is also shown in Fig. 7.

that they have been introduced into the crystal at different times. The wider set, Y, corresponding to the diffraction pattern observed, extends over much of the crystal flake, suggesting that they formed initially and at high temperatures. This accounts for the fact that they are straight and well ordered. The set X which terminates is less well ordered and seems to have grown into the crystal after the first set. The disorder in these latter CS planes suggests that long annealing times and high temperatures were not available after their formation and it is possible that they are the result of beam heating of the crystal flake before observation began.

Figure 6 shows a complex twinned region in another fragment from a large WO_{3-x} crystal. The CS planes, which are on (301) and $(\bar{3}01)$ planes, are seen to stop in some places and at others are turned through 180°. At these bends, octahedra are necessarily linked in units different from the block of 6 normally found in the {103} CS plane. Figure 7 shows an interpretation of part of Fig. 6 in which these alternative linkages are employed. As before, only the CS planes are drawn and distortions of the matrix near the twin boundaries and elsewhere have been ignored.

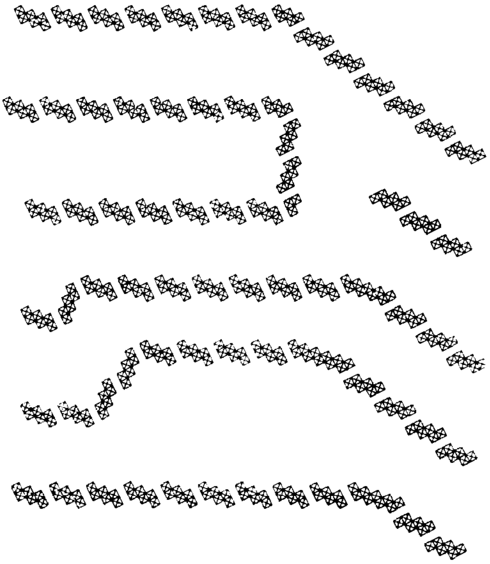

FIG. 7. Idealized representation of the structure of the region of Fig. 6 enclosed in a box. Only the linkage of the octahedra in the CS planes is shown; the WO_3 matrix being omitted for clarity.

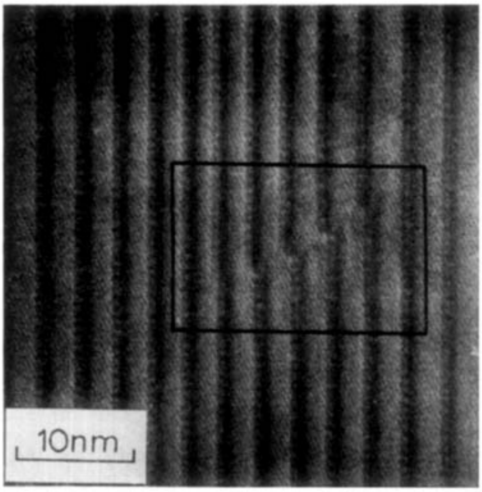

FIG. 8. Lattice image showing $(\bar{2}01)$ CS planes in a fragment of a large WO_3 crystal reduced at 950°C. The area in the box is also shown in Fig. 9.

Large WO_3 Crystals Heated at 950°C

When large crystals were heated at the rather lower temperature of 950°C, the defect structure was found to be different. The oxygen loss was now accommodated on {102} planes. In many parts of the crystal these are quite

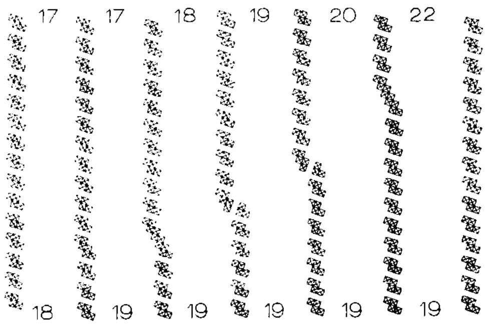

FIG. 9. Idealized representation of the structure of the region of Fig. 8 enclosed in a box. Only the linkage of the octahedra in the CS planes is shown; the WO_3 matrix being omitted for clarity. The numbers between each CS plane refer to the value of n in the formula W_nO_{3n-1} which expresses the composition of these oxides.

well ordered and form regions of W_nO_{3n-1} phases. The value of n has been found to run from approximately 12 to 24 in these crystals. Figure 8 shows such a well ordered region containing ($\bar{2}01$) CS planes with $n \simeq 19$ and composition approximately $WO_{2.95}$. The octahedral groups within the CS planes are not resolved but the detail is sufficiently clear to allow possible structures for the slight faulting shown in Fig. 8 to be derived. One such possibility is shown in Fig. 9. It is seen that in this faulted region more octahedra are linked in the edge-shared groups than in the unfaulted CS planes, and therefore a slightly greater degree of reduction pertains here.

A feature much more commonly met with in these crystals is the presence of relatively isolated {102} CS planes. They seem to occur whenever the CS planes are not reasonably well ordered, and occupy much of the unchanged matrix. Such an effect is illustrated n Figs. 10a and b, which show a region between 2 slabs of crystal containing fairly well ordered CS planes lying on ($\bar{2}01$) and ($\bar{1}02$) planes. The way in which the CS planes link, with bent and curved regions, such as at A in Fig. 10a, suggests that groupings of octahedra other than 4 occur in places. In addition a number of short segments of CS plane can also be seen which do not lie on {102} planes. These segments are too short to allow precise indices to be derived and the resolution of the prints does not allow the sequence of edge-shared WO_6 octahedra in the CS planes to be determined. One can, however, again conclude that such CS planes contain constituent groups of edge-shared octahedra which differ from the group of four normally found in {102} CS planes.

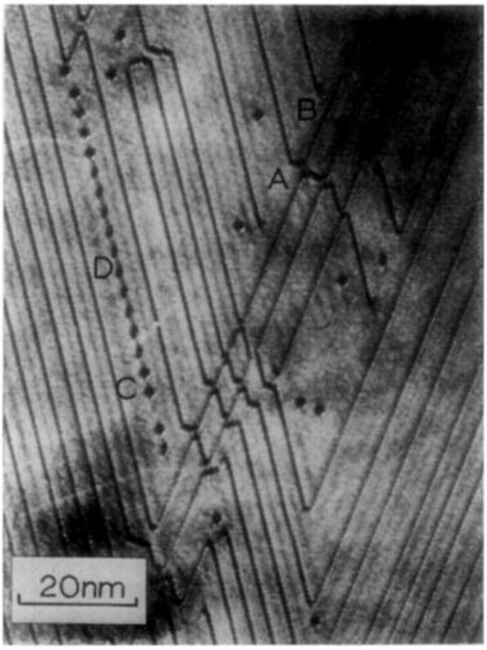

FIG. 10(a). A fragment of a large WO_3 crystal reduced at 950°C containing CS planes on ($\bar{2}01$) planes (left) and ($\bar{1}02$) planes (right). Curved CS planes (e.g., at A) and terminating CS planes (e.g., at B) are also present and two other defects at C and D.

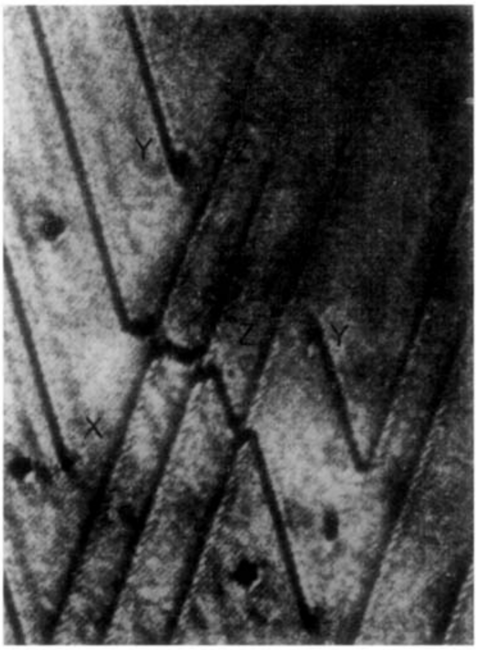

FIG. 10(b). Enlargement of part of (a) showing the interaction of the terminating CS planes Y with the CS planes Z.

There is a certain amount of interaction between these CS planes which is revealed in Fig. 10a at B and more clearly in Fig. 10b. The 2 CS planes Y in Fig. 10b stop in the crystal and the 2 CS planes Z are seen to curve slightly at the point nearest to Y. The separation between the CS planes Y and Z is approximately 2.2 nm. At X the effect is similar, but much less severe, as the separation between the interacting CS planes has increased to approximately 3.3 nm.

A prominent feature of these same regions is the presence of star-shaped defects, both isolated and quasiordered. There are 2 different types of features, indicated by C and D in Fig. 10a. At present their interpretation is uncertain, but they have not been seen to occur in regions of crystal containing fairly close, well ordered {102} CS planes, or in crystals containing a {103} CS structure. Further studies are needed to clarify the nature of these faults.

Large WO_3 Crystals Heated at 1000°C

The results described above showed that at temperatures of 950°C the crystals supported oxygen loss by the formation of {102} CS planes, while at 1070°C, crystals contained {103} CS planes. It was, therefore, considered necessary to examine crystals heated between these temperatures to determine the nature of their defect structure.

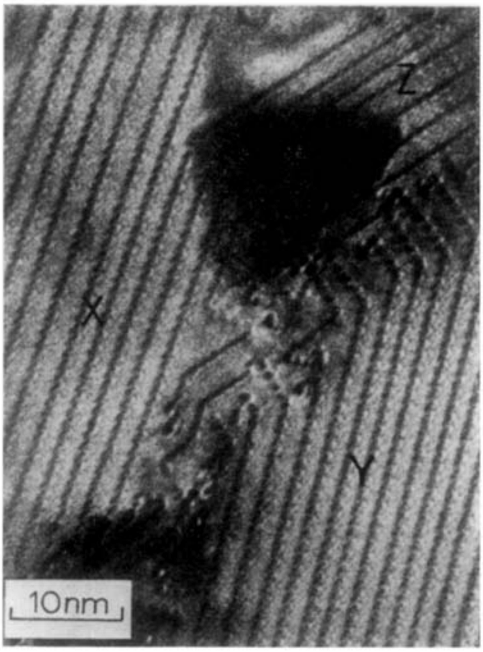

FIG. 11. Lattice image of a fragment from a large WO_3 crystal reduced at 1000°C. The CS planes are on (301) planes in the region X, (201) planes in the region Y, and $(\bar{3}01)$ planes in the region Z.

Electron microscope examination of a crystal heated at 1000°C showed it to be inhomogeneous with a large composition difference existing between the outside and the middle. The outer parts, after being freed of needle crystals, contained {103} CS planes. The average composition of this material was $WO_{2.89}$. The centre, on the other hand, showed disordered {102} CS planes, or regions of ordered {102} CS planes rather similar to crystals of composition $WO_{2.99}$ examined in a previous study (*7*). Fragments of crystal which were taken from some small distance inside the outer surface were found to contain both {102} and {103} CS planes. Figure 11 shows such regions separated by a rather complex boundary of kinked CS planes. The region X was identified as containing (301) CS planes from a correct orientation of the diffraction pattern from the flake with the micrograph. The CS planes in region Y are at an angle of 6° to those in region X. It is not possible to consider the region Y as also containing (301) CS planes as this angle is too large to be due to subgrains in the monoclinic WO_3 lattice, 1–3° (*5*). A consideration of the reciprocal lattice suggests that they are (201) CS planes, although the ideal angle between these two sets of CS planes should be 8°. No other plane with relatively simple indices presents itself as a likely alternative. The assignments made for regions X and Y allow the CS planes in region Z to be indexed as $(\bar{3}01)$. The region between X, Y and Z contains principally (103) and $(\bar{3}01)$ CS planes, but a closer inspection reveals that a number of these short CS plane segments are not parallel to their neighbours. Their shortness makes interpretation of their indices imprecise, but signifies that the edge-shared octahedral units comprising the CS plane must vary from the group of 6 found in {103} CS planes.

A measurement of the CS plane separation in regions X and Y shows a spacing of about 2.2 nm, corresponding well with the diffraction pattern, which suggests that the (301) component of the CS phase is $W_{18}O_{52}$ or $W_{19}O_{55}$. These have CS plane separations of

2.115 nm and 2.233 nm, respectively. As this spacing is preserved in the (201) region, the composition must be higher, changing from approximately 2.89 in region X to 2.92 in region Y. This corresponds to an oxide of approximate formula $W_{13}O_{38}$.

Discussion

In the present series of experiments crystals of needle habit were always found. Previous studies suggested that they contained {103} CS planes and that the mechanism by which these needles formed was one in which vapour transport was involved. Both of these suppositions have been verified in the present experiments. The observation of needle growth on parts of the silica tubes several centimetres away from any of the original tungsten or tungsten trioxide starting materials indicated that vapour transport was important in their growth. Structurally these needle crystals always appeared to consist of {103} CS phases and in most respects they seem to be identical to the materials examined by Allpress and Gadó (*5*) although the extreme disorder occasionally found by these authors was not observed in the present study. The conclusions to be reached are that, in the limited temperature range involved in this work, needle shaped crystals have grown from the vapour phase and contain quasiordered {103} CS planes.

In contrast to this the way in which large tungsten trioxide crystals supported their oxygen loss was quite temperature dependent, and {102} or {103} CS planes were found, depending on preparation conditions. The {103} CS phases found in the large crystals appeared to be very similar in microstructure to those seen in the crystals of needle habit. The {102} phases were somewhat different in that rather open regions occurred with a low density of CS planes, typified by Fig. 10. This difference is probably due to the generally lower degree of reduction of the {102} containing matrix. Such regions usually showed small star shaped features. Their occurrence was restricted to the open regions between CS planes suggesting that they are associated with the nucleation or annihilation of CS planes. However, this must be regarded as speculative until contrast experiments have clarified their true nature.

Within such open regions of the crystal, nonparallel CS planes can approach one another closely. This behaviour is also illustrated in Fig. 10 where an interaction between terminating and continuous CS planes is revealed. This occurs where a CS plane has approached to within a few nm of an essentially continuous CS plane. The slightly distorted shape of the continuous CS plane must reflect any forces arising from the dislocation which bounds the terminating CS plane and the distortion of the WO_3 structure which necessarily accompanies the dislocation. In the present case the appearance of the CS plane suggests that a repulsive force is operative over a range of up to 3 nm. The results included here are not sufficient to allow a detailed analysis of the force to be made. However, the existence of such a repulsive effect does explain in a satisfactory way why CS planes in such open regions of crystal seem not to intersect each other very often. Instead one or other of the CS planes appears to be deflected into a twinned orientation resulting in the complex array of bends typified by Fig. 10. This deflection appears to take place when the CS plane pair are separated by between 1 and 2 nm. A similar interaction would be expected in (103) materials and would be a possible cause of the hairpin configurations seen at twin boundaries in (103) CS phases. An examination of Figs. 3 and 6 reveal that the CS planes in these materials approach each other in this oblique fashion to a similar distance of 1.5 nm before turning aside to form a hairpin or stopping.

The situation in which nonparallel CS planes interact should be distinguished from that in which parallel CS planes interact, which is likely to be somewhat different. Information on the forces between parallel CS planes in slightly reduced tungsten trioxide is not yet available and a comparison is not possible. However, Bursill and Hyde (*13*) have considered the forces between parallel CS planes in reduced rutile and have found that at distances of approximately 2 nm only a rather weak attraction occurs. The existence of the wide and narrow CS plane pairs of the type shown in Fig. 5 suggests that the situation in these oxides is rather similar to that in rutile. If a strongly repulsive force dominated the CS plane array, a regular sequence of CS planes would be expected. Other factors, however, must be important in controlling the particular spacings found, which in Fig. 5 shows a division of $W_{23}O_{67}$ into unequal parts of $W_{10}O_{28}$ and $W_{13}O_{37}$.

In the W_nO_{3n-2} homologues, the displacement of the tungsten atoms from the centres of the WO_6 octahedra varies from one to another (*1*, *2*). Magnéli (*14*) has suggested that the distortion patterns found in the tungsten oxide CS phases might play an important part in conferring greater stability on particular members of a homologous series. Hence the subdivision revealed in Fig. 5 might be due to the greater preferred stability of one or both of the homologues formed over a pair of equal spacing. Alternatively, the tungsten atom puckering in the WO_3 strips between the wide spaced set of CS planes might dispose the material to favour the particular subdivision found as further reduction took place, if as was suggested, the CS plane set X were introduced after the set Y. The limited amount of experimental evidence available does not allow more firm conclusions to be drawn, as the actual conditions prevailing in the crystal during CS plane formation are unknown.

The nature of the CS plane type found in the large WO_3 crystals seems to be a function of composition and temperature. At present the experiments do not allow the limits of existence of {102} and {103} CS planes to be delineated at 950°C and 1070°C. At 1000°C where {102} and {103} CS planes were found to coincide, the situation is understood in rather more detail. At this temperature $W_{12}O_{35}$ and $W_{13}O_{38}$ of the {102} series were found to coexist with $W_{18}O_{52}$ and $W_{19}O_{55}$ of the {103} series. Greater reduction than this is accommodated on {103} CS planes and homologues with n less than 18 are found, while compositions greater than $W_{13}O_{38}$ are accommodated on {102} CS planes.

This situation is remarkably similar to that occurring in the titanium oxides. Small degrees of reduction of rutile, TiO_2, are accommodated on $\{132\}_r$[2] CS planes down to approximately $Ti_{16}O_{31}$ ($TiO_{1.938}$), while below this $\{121\}_r$ CS planes take over, starting at compositions of approximately $Ti_{10}O_{19}$ ($TiO_{1.90}$) and continuing to Ti_4O_7. Original studies suggested that in the phase range $TiO_{1.938}$–$TiO_{1.90}$, $Ti_{16}O_{31}$ of the $\{132\}_r$ series coexisted with $Ti_{10}O_{19}$ of the $\{121\}_r$ series. It was significant that the CS plane spacing in $Ti_{16}O_{31}$ was very close to that in $Ti_{10}O_{19}$, approximately 1.6 nm. In the present study analogous features were found. The homologues of the 2 series which coexist, $W_{13}O_{38}$ of the {102} series and $W_{18}O_{52}$ of the {103} series, do not have similar compositions, but almost identical CS plane spacings. In this case the approximate spacings are 2.125 nm and 2.115 nm, respectively.

A more careful appraisal of the TiO_{2-x} system in the phase range $TiO_{1.938}$–$TiO_{1.90}$ showed that ordered series of parallel CS planes were found with indices between $\{121\}_r$ and $\{132\}_r$ and that intermediate compositions were not 2 phase mixtures of $\{121\}_r$ and $\{132\}_r$ CS phases in the conventional sense (*8*). In fact, the $\{121\}_r$ and $\{132\}_r$ components have intergrown on an atomic scale to form intermediate CS plane indices, and new homologous series of oxides. The same situation is likely to hold in the present case. The observation of short lengths of CS planes with an orientation between {102} and {103} suggests that in favourable conditions, ordered phases based upon CS planes lying between {102} and {103} will be found.

At present there are insufficient experimental data available to enable one to specify the factors which control the change of CS plane type from {102} to {103}. However, the metal atom puckering which occurs in these compounds and which may have a role to play in the stability of various members of a homologous series (*14*) may also influence the linkage of octahedra which are found in the CS plane. This metal atom puckering has already been shown to be composition dependent, as it varies from one member of a homologous series to another (*1*, *2*, *14*).

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[2] The subscript r refers to indices of CS planes in the rutile structure.

Moreover, the off-centre displacements of the tungsten atoms in tungsten trioxide are known to be temperature dependent and this is likely to hold true in the CS phases as well. Such behaviour could possibly then lead to the temperature and composition dependence of CS plane type noted. The mechanism by which this could come about, is, however, obscure.

The information presented in this paper has shown that the way in which the WO_3 lattice accommodates oxygen loss is a function of composition and temperature. Hence, to determine beforehand whether the defect structure of WO_3 will be based upon {102} or {103} CS, both of these parameters should be specified. Occurrence of elements of CS plane with orientation between {102} and {103} suggests that curved CS plane surfaces may be found, or new homologous series of oxides based upon ordered (*h*0*l*) CS planes with indices lying between {102} and {103}. A more extensive set of experiments is now under way to determine the extent to which these speculations are correct. At the same time, a careful determination of the {102} and {103} phase boundary is being made as it is only when such data are available that the factors which control the formation of a particular CS plane type will be open to investigation.

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