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The Elastic Strain Energy of Crystallographic Shear Planes in ReO_3-Related Oxides. II. *CS* Plane Arrays

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The elastic strain energy of the matrix lying between pairs of crystallographic shear (*CS*) planes in the ReO_3 type structure has been calculated as a function of *CS* plane spacing and *CS* plane type. The *CS* planes considered are {104}, {105}, {106}, {107}, and {001}, and in addition the results for {102} and {103}, reported previously are included. These results are used to discuss and explain the relative stabilities of differing {10*m*} *CS* plane arrays and also the relative stabilities of members of the homologous series generated by ordered arrays of these *CS* planes. The microstructures of arrays of *CS* planes that may occur in reduced binary or ternary tungsten oxides, which are slightly distorted variants of the ReO_3 type, and in NbO_2F which has the ReO_3 structure are also considered.

Introduction

The crystallographic shear (*CS*) structures resulting when the ReO_3 (DO_9) related materials WO_3 and NbO_2F are reduced have been the subject of much research. It is well known that initial reduction of WO_3 results in isolated *CS* planes on {102}[1] planes and at greater degrees of reduction arrays of ordered or partly ordered *CS* planes are found on {103} planes. If WO_3 is reacted with Nb_2O_5, *CS* plane arrays also form on {104} and {001} planes. Reduction of NbO_2F, on the other hand, leads only to Nb_3O_7F, containing an ordered array of {001} *CS* planes. These results, and others of importance, are surveyed in a number of review articles (*1–5*).

In an attempt to analyze the large amount of information concerning the microstructure of the *CS* phases several authors have attempted to assess the interaction energy between pairs or arrays of *CS* planes. The first of these were Bursill and Hyde (*6*), who proposed a qualitative form for the interaction energy between two parallel *CS* planes in reduced rutile, (TiO_{2-x}), but did not specify the origin of the forces. They expanded this idea in a discussion of WO_3-derived *CS* structures (*7*) and suggested that *CS* plane interactions could be divided into an inter-*CS* plane component, and an intra-*CS* plane component. The inter-*CS* plane interactions were supposed to change with *CS* plane separation from attractive to repulsive, while the intra-*CS* plane interactions depended upon the ratio of antiphase boundary to collapse steps within each

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[1] Throughout this paper the WO_3 *CS* plane indices are referred to an idealized cubic cell of the DO_9 (ReO_3) type.

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CS plane. These ideas, though, were not treated quantitatively and the origins of the interactions were not specified.

Stoneham and Durham (*8*) proceeded further than this, and calculated the elastic strain energy between a pair of parallel {001} *CS* planes in an idealized ReO_3 matrix. In this treatment, the forces causing the strain were supposed to arise in the *CS* plane due to interactions between the ions within the *CS* plane. The matrix between the *CS* planes was considered to transmit the forces from one *CS* plane to the other. They also made an estimate of the electrostatic interaction energy between the *CS* planes.

The present authors have made further progress in a quantitative understanding of these interactions. First, the elastic strain energy in the matrix surrounding isolated pairs and arrays of {102}, {103}, and {001} *CS* planes in an idealized cubic WO_3 lattice has been calculated (*9*). It was found that many of the microstructures to be observed in WO_{3-x} crystals containing *CS* planes could be explained by assuming that configurations with minimum elastic strain energy were preferred. Second, electrostatic interactions were calculated for the same *CS* plane types (*10*) and it was shown that this energy was negligible compared to the elastic strain because of the large value of the dielectric constant of WO_3. Neither of these results is able to explain why, on reduction of WO_3, the sequence of *CS* plane arrays {102} → {103} → {104} → {001} is observed as reduction increases, nor why *CS* plane arrays with indices greater than {104} have not been observed. In a similar way it is unable to explain the preference of NbO_2F for only {001} *CS* planes.

In an attempt to answer these questions Iguchi (*11*) has evaluated the absolute magnitude of the elastic strain energy, and Tilley (*12*) has considered the formation energy of {10*m*} *CS* planes in a qualitative way. Iguchi and Tilley have considered this formation energy more quantitatively and these considerations form Part I of this paper (*13*). The present paper continues the calculations described above by evaluating the elastic strain energy in an idealized cubic ReO_3 matrix containing arrays of {10*m*} *CS* planes, where *m* takes values from 4 to 7 and also ∞. These results are discussed in terms of the microstructures found in the niobium oxyfluorides and tungsten oxides.

CS Structures

The WO_3 derived *CS* structures have been described at length in many of the publications referred to in the Introduction (see especially (*1–3*, *9*, *12* and references therein)) and will only be described very briefly here. Tungsten trioxide itself is built up of an infinite array of corner-sharing octahedra, which, in reality, are somewhat distorted, and lower the symmetry of WO_3 from a cubic form isostructural with ReO_3 and possessing the DO_9 structure to monoclinic.

A *CS* plane in reduced WO_3 can be imagined as a plane along which the crystal has collapsed so that the corner-sharing octahedra have become linked by edge sharing instead. They can be constructed geometrically by removing a plane of oxygen atoms and rejoining the separated crystal halves so that no oxygen positions remain empty. Figure 1 shows representations of idealized WO_3 and some of the {10*m*} *CS* planes discussed in this paper, all of which have been idealized somewhat by making all the octahedra regular instead of slightly distorted as they are in practice. Other diagrams will be found in the preceding paper (*13*).

If a reduced WO_3 crystal contains an ordered array of parallel {10*m*} *CS* planes, its overall stoichiometry will be given by $W_nO_{3n-(m-1)}$, where *n* specifies the number of octahedra between the *CS* planes in a direction parallel to the *c* axis, as shown for a {104} *CS* plane in Fig. 2. The composition of the reduced crystal, *x*, in the formula WO_x, will be given by

$$x = 3n - (m - 1)/n \tag{1}$$

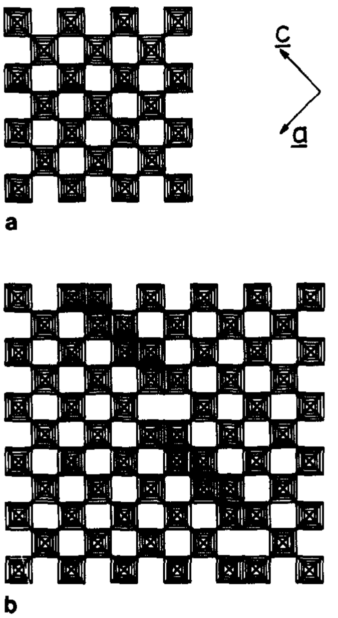

FIG. 1. Idealized representations of (a), the ReO_3 structure which is the same as as idealized WO_3, (b) a {104} *CS* plane. The shaded squares represent (MO_6) octahedra. The crystallographic *a* and *c* axes are also indicated.

and the spacing between *CS* planes in a crystal of overall composition *x*, d_x, is given by

$$d_x = \frac{a[2n - (m - 1)]}{\{2[(m - l)^2 + (m + 1)^2]\}^{1/2}}. \qquad (2)$$

The composition of a crystal can be changed by altering *n*, the separation of the *CS* planes, in which case a homologous series of oxides of general formula $W_nO_{3n-(m-1)}$ is formed. Alternatively, if the orientation of the *CS* plane, represented by *m*, changes, the composition can change while the *CS* plane spacing remains virtually unaltered. In practice the real microstructures of reduced crystals show disorder and a variety of spacings occur between parallel *CS* planes and on occasion different *CS* plane orientations are also found in crystals.

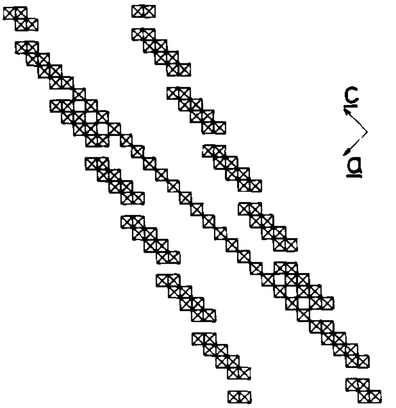

FIG. 2. A diagrammatic representation of a {104} *CS* plane pair. The *n*-value of this pair is 28. The crystallographic *a*- and *c*-axes are indicated.

Calculations and Results

$(U_s)_2$

In this report we have calculated values for $(U_s)_2$, the elastic strain energy between a pair of parallel *CS* planes. These results are then used to estimate the elastic strain energy per unit volume of ordered arrays of *CS* planes in a similar fashion to that employed in our previous report (*9*). The *CS* planes considered here have indices {10*m*} where *m* takes values between 4 and 7, and also ∞. To do this we have used classical elasticity theory; the method of calculation following the treatment by Hirthe and Lothe (*14*). This has been described in detail for {102} and {103} *CS* planes (*9*). The method employed here for the other {10*m* } *CS* planes follows that exactly and will not be elaborated here. It should, however, be noted that we have made a number of simplifying assumptions. These are, first, that the crystal structure of WO_3 has been taken to be of the idealized cubic ReO_3 (DO_9) type, with a lattice parameter, *a*, of 0.38 nm. All *CS* plane indices are referred to this unit cell. Second, we assume that the crystal can be treated as an isotropic continuum except in the region of the *CS* planes, which are considered to contain discrete ions.

Following the procedures detailed in (*9*) we have calculated the elastic strain energy in the matrix between a parallel pair of {10*m*} *CS* planes, per unit area of *CS* plane. This is defined as $(U_s)_2$. The strain of any ion between a pair of *CS* planes should ideally be

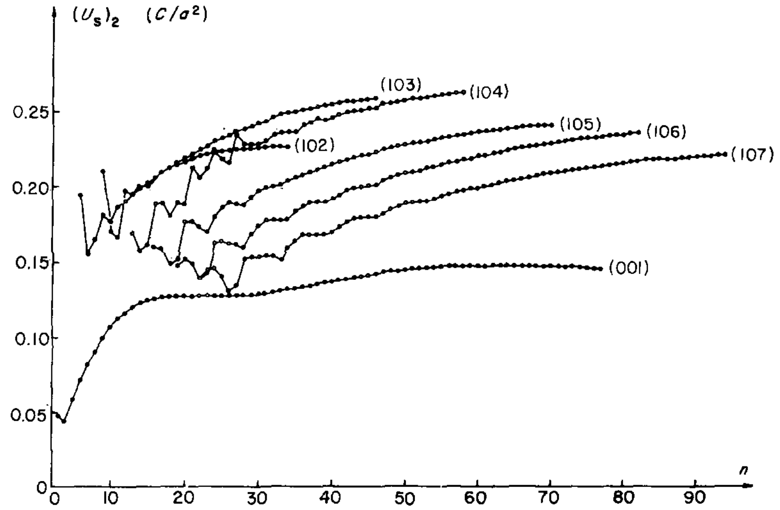

FIG. 3. The elastic strain energy $(U_s)_2$ between a pair of {102}, {103}, {104}, {105}, {106}, {107}, and {001} *CS* planes, in units of (C/a^2), as a function of the number of (MO_6) octahedra, *n*, between them, where $C = (\lambda + 2\mu)(f/8\pi\mu)^2(4\pi r_0^3/3)$ and *a* is the lattice constant. The vertical axis represents $(U_s)_2$ and the horizontal axis *n*.

the summation of the strains due to all of the units of blocks of edge-shared pairs of octahedra in the *CS* planes *1* and *2*, but as this is impractical, in making the calculations we have chosen to sum the strains due to 17 × 41 units in the case of {104} *CS* planes, 15 × 41 units in the case of {105} *CS* planes, 13 × 41 units in the case of {106} *CS* planes, and 11 × 41 units in the case of {107} *CS* planes. In the case of {001} *CS* planes, which are equivalent to {10∞} *CS* planes, it is impractical to calculate the terms exactly. Therefore we have made the approximation that a unit of a {10,85} *CS* plane is equivalent to a unit of an {001} *CS* plane, and calculated the strain due to a block of 1 × 41 units in this structure. This block has the same area as those for the other {10*m*} *CS* planes. As the method of calculation for {001} *CS* planes in this report is different from that in our previous paper (*9*), the magnitudes of $(U_s)_2$ for {001} *CS* planes differ slightly from those published before, but this difference is too small to change the overall situation greatly. We have employed this treatment in this paper because it is more consistent with the calculations for the other {10*m*} *CS* planes. It was found that the absolute value of the ratio of the strain due to a unit in the boundary of these blocks to the strain due to a unit in the center (which gives the largest strain) was less than 0.01.

Naturally it is to be expected that $(U_s)_2$ will depend upon the spacing between the *CS* planes. Thus in Fig. 3 we have shown $(U_s)_2$ as a function of *n* which is the value in the formula $(M, \mathrm{W})_n\mathrm{O}_{3n-(m-1)}$ generated if we had an array of *CS* planes instead of just a single pair. The values for {102} and {103} *CS* planes, reported elsewhere (*9*), are also included in this figure.

The Elastic Strain Energy of an Ordered Array of CS planes

If a crystal has a composition *x*, equal to $3n - (m-1)/n$, due to an ordered array of {10*m*} *CS* planes then the increase in elastic strain energy per unit volume due to the $(U_s)_2$ component of the elastic strain energy of the ordered *CS* plane array will be given by (U_x/L). The number of *CS* planes introduced into the crystal, N_x is related to the spacing between the *CS* planes, d_x and *L* by the equation

$$N_x d_x = \mathrm{L}. \qquad (2)$$

(U_x/L) can then be written as

$$(U_x/L) = (N_x - 1)(U_s)_2/L + (U_s)_1/L, \quad (3)$$

where $(U_s)_1$ is the elastic strain energy of the matrix surrounding a single isolated $\{10m\}$ *CS* plane

$$= (N_x - 1)(U_s)_2/N_x d_x + (U_s)_1/N_x d_x \quad (4)$$

and as we are supposing N_x to be high, i.e., $N_x \gg 1$,

$$(U_x/L) = (U_s)_2/d_x. \quad (5)$$

We should note here that we have ignored elastic strain within the *CS* planes themselves, and are also only concerned with the strain in the matrix between *CS* planes. Moreover in our treatment, interactions between *CS* planes other than nearest-neighbor interactions have not been considered at this stage, as our preliminary results, ignoring these cumulative effects, appear to be in fair agreement with experiment (*9*). At present calculations involving interactions other than just nearest-neighbor interactions are under way and will be reported in the future.

The elastic strain per unit volume due to $(U_s)_2$ in a crystal containing an ordered array of *CS* planes is given by Eq. (5). As the spacing between the *CS* planes at any composition of the crystal x is not of such importance as the relationship between the elastic strain and the overall composition of the crystal we have plotted in Fig. 4 $(U_s)_2/d_x$ vs composition x. We have, as for Fig. 3, also included in this figure the values of $(U_s)_2/d_x$ for $\{102\}$ and $\{103\}$ *CS* planes calculated previously (*9*). We should also point out here that the numerical values for $(U_s)_2/d_x$ reported here are slightly different from those in (*9*) as here we have expressed d_x in terms of a, the WO_6 octahedron diagonal rather than directly in nanometers. The values in (*9*) can be equated with these given in Fig. 4 simply by dividing by $2^{1/2}$. This does not affect the trend shown in Fig. 4 and is of no significance in the discussion that follows.

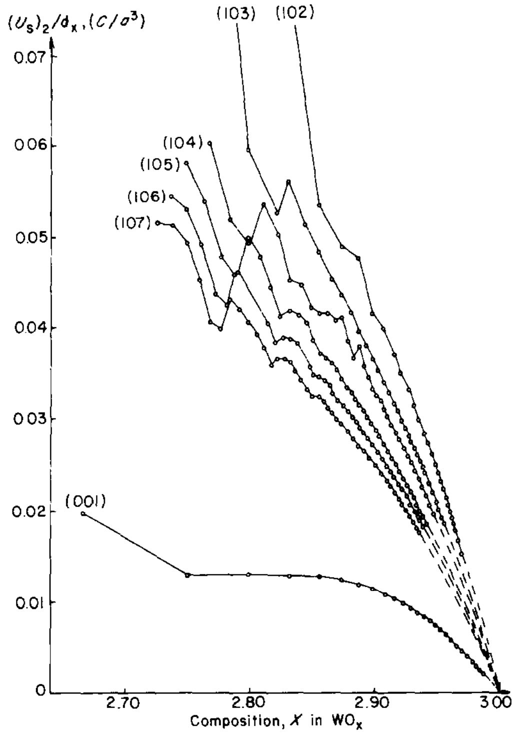

FIG. 4. The elastic strain energy per unit volume $(U_s)_2/d_x$ for an ordered array of $\{102\}$, $\{103\}$, $\{104\}$, $\{105\}$, $\{106\}$, $\{107\}$, or $\{001\}$ *CS* planes plotted as a function of the composition of the crystal x in MO_x. The vertical axis represents $(U_s)_2/d_x$ and the horizontal axis x in MO_x. Some of the theoretical points have been omitted from the part of the curves at higher x values for clarity. The broken lines are extrapolated ones.

Discussion

Before we consider the significance of the elastic strain energies calculated in this report it is useful to consider some more general aspects of the approach employed. First, it would seem reasonable, on chemical grounds, to assume that forces, f, exist within the *CS* plane arising from the bonding between the atoms. Clearly these may be attractive or repulsive and the matrix between the *CS* planes will then be either under tension or compression. The magnitude of the elastic strain energy depends upon f^2, and as such whether the matrix is in tension or compression is not vital, as similar energy values result in either case. For our purposes, an ionic model using repulsion between cations seemed the most reasonable first model to take. Should the results of the calculations be at variance with the experimental data, more elaborate models could be exploited. However, the results obtained so far suggest that this is not necessary.

For somewhat similar reasons we have assumed that the forces in the *CS* plane decay in an inverse square ($1/r^2$) fashion with distance. The most logical alternative is to use a simple inverse ($1/r$) relation, which is generally assumed to hold for the forces around a dislocation core. We have, in fact, also tried such a model, but it had a number of shortcomings, the most important of which was that it did not allow a clear distinction to be made between the crystallographic structures of $\{10m\}$ and $\{10, m + 1\}$ *CS* planes. For this reason and others the $1/r$ force model was abandoned. Further calculations for $\{001\}$ *CS* planes (Iguchi, to be published) suggests that the force actually varies in a rather complex manner and that although the $1/r^2$ dependence is a much more reasonable approximation than $1/r$ dependence, neither is exactly correct. The differences this would make are likely to be important in understanding the fine details of the microstructures, but not so important in considering the broader aspects discussed here.

Another point of interest concerns the applicability of calculations involving the idealized cubic ReO_3 structure to WO_3 which has a slightly distorted ReO_3-type structure. The source of the distortions in WO_3 are not clear, although a number of factors will be of importance. These are most likely to involve the bonding between the cations and anions, and also the small size of the W^{+6} cations, which in itself will favor an off-center environment for the W ions in their coordination octahedra. In addition, elastic strain and relaxation may also contribute to the observed distortions. These factors, though, should not be overemphasized, as at the temperatures at which most of the *CS* phases are prepared the distortions will be considerably less than at low temperatures, and moverover the lattice will not be static but vibrating appreciably. This suggests that the average structure at high temperatures will be fairly well approximated by an ReO_3 type of model.

Analytically we can say that if we write the strain energy of an ion at r in ReO_3 as $w(r)$, in WO_3 we must write $w(r + \delta r)$, where δr is the term representing the distortion of the WO_3 structure relative to the ReO_3 structure. We can therefore approximate the strain in the WO_3 structure to $w(r + \delta r) = w(r) + \delta r w'(r)$. As δr will be small, $w(r) \gg \delta r w'(r)$ and we expect the two strain energies to be very similar. In fact our numerical calculations show that the strain of an ion at r is not very different from that of its nearest neighbor at $r + a$, and for this reason, the extrapolation of our results to WO_3 seems perfectly reasonable. We can therefore apply the $(U_s)_2$ terms both to an ReO_3 structure material such as NbO_2F or to the slightly distorted WO_3 with a fair degree of confidence.

As can be seen from Fig. 3 the value of $(U_s)_2$ is smallest for $\{001\}$ *CS* planes and greatest for $\{102\}$ *CS* planes. In addition, all the curves show, to some extent, a series of maxima and minima, although this is hardly pronounced in the case of $\{001\}$ *CS* planes. In practice, the strains from each *CS* plane will either tend to add together or to cancel each other depending upon the relative dispositions of the blocks of edge-sharing octahedra in the two *CS* planes. If the pairs of *CS* planes are drawn it will be found that the relative dispositions of these units is periodic, and depends upon the separation of the *CS* planes, n. For $\{102\}$ *CS* planes the same relative disposition occurs every other n value, for $\{103\}$ *CS* planes at $n = n + 3$, for $\{104\}$ *CS* plane at $n = n + 4$ and in general for $\{10m\}$ *CS* planes at $n = n + m$. Clearly in one of these dispositions the strains will cancel and so yield a minimum every $n + m$, while at one disposition the strain will add to yield a maximum every $n + m$. Thus the $(U_s)_2$ curves would be expected to have a series of maxima and minima with a periodicity *m* as is shown clearly in most of the curves of Fig. 3. For {105}, {106}, and {107} *CS* planes the minima occur when the space between two units of edge-shared octahedra in *CS* plane *1* coincides with the middle of the block of edge-shared octahedra in *CS* plane *2*. For {102}, {103}, and {104} *CS* planes this criterion is not true. It would therefore seem that as the units of edge-shared octahedra get longer the position of minimum strain becomes easier to define and is associated with an "out-of-phase" positioning of the *CS* planes but this simple situation fails as the block size decreases.

Relative Stabilities of {10m} CS Plane Arrays

The $(U_s)_2$ results can be used to discuss the microstructures to be expected in arrays of *CS* planes. First, we will consider which array of *CS* planes is likely to be stable at any given composition, WO_x. As we have stated in Part I we can divide the energy terms into parts, and so we can say that the excess internal energy of a crystal containing an ordered array of {10*m*} *CS* planes over and above that of the original WO_3 matrix will consist of the energy of formation of the {10*m*} *CS* planes and the interaction between them.

Part I of this communication shows that the formation energy of a {10*m*} *CS* plane is lowest for the {102} *CS* geometry, passes through a maximum for {104}, and then drops to a low value for {001} *CS* planes. The interaction energy will be divided into the elastic strain energy $(U_s)_2$, a coulomb interaction between the *CS* planes and the surrounding matrix $(U_e)_2$ and if the *CS* planes are not neutral, a repulsive coulomb energy (U_{rep}). In general, except perhaps at very close separations, the *CS* planes can be regarded as neutral, making (U_{rep}) zero. Moreover $(U_e)_2$ is negligibly small compared with $(U_s)_2$. (*8–10*). Thus we can take the *CS* plane energy as simply the sum of the formation energy and the elastic strain interaction energy $(U_s)_2$.

Figure 4 shows the elastic strain energy per unit volume, $(U_s)_2/d_x$, for a variety of arrays between {102} and {001}. In general, at any composition *x*, the elastic strain interaction energy is lowest for {001} *CS* planes and highest for {102} *CS* planes. This allows us to draw two conclusions. In the case of NbO_2F it is known that initial reduction leads to the formation of random {001} *CS* planes (*6*). Clearly, as these become closer, and interactions become important the formation of an ordered array of {001} *CS* planes would be expected. The formation of an array of any other {10*m*} *CS* planes would lead to an increase in the total energy of the system and would be most unlikely.

In WO_3, on the other hand, initial reduction leads to the formation of {102} *CS* planes. At low *CS* plane densities the $(U_s)_2$ term would be negligible. However, as the *CS* plane population increases, the $(U_s)_2$ interaction will become increasingly important. Unlike NbO_2F, we now have two opposing energy terms. Formation energy would prefer {102} while the $(U_s)_2$ interaction would favor an {001} *CS* plane geometry.

As we have discussed previously (*12*) the interaction will increase as the *CS* plane density increases, and at some value a change from {102} to another *CS* plane type will become favorable. As the formation energy of {10*m*} *CS* planes has its minimum value when $m = 2$, and passes through a maximum, m_{max}, at $m = 4$, before falling to the value for $m = \infty$, applicable to {001} *CS* planes, we suppose that the transition {102} → {103} → {104} needs energy. This may be supplied by $(U_s)_2$ and at some value of *CS* plane density a {102} array may change to a {103} array and gain energy in doing so. That is, above some critical composition the {102} array will have a higher free energy than a {103} array. As the composition falls the {102} array will give way to a {103} array. We would expect the same thing to happen on further reduction and {103} *CS* planes should give way to {104} *CS* planes. However, if the formation energy

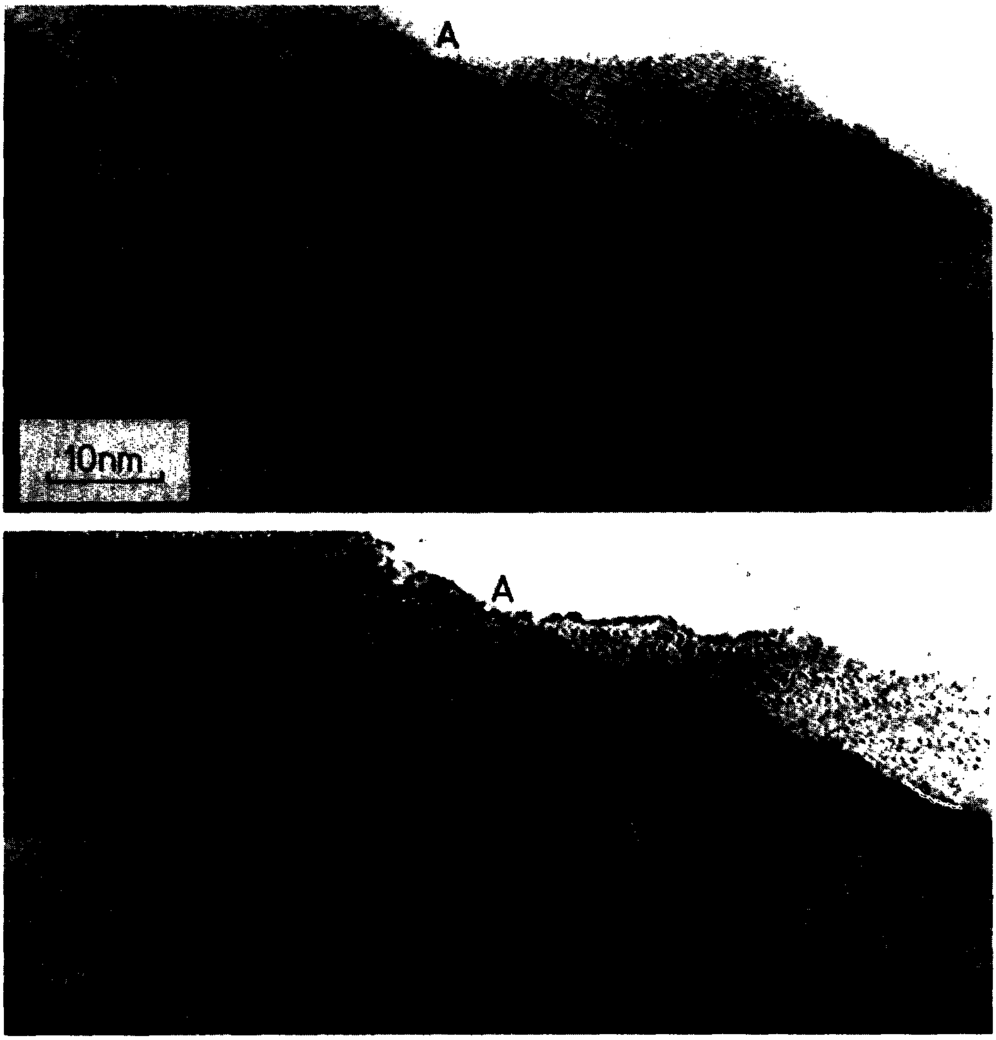

FIG. 5. (a) Electron micrograph of a crystal fragment of slightly reduced WO_3 containing *CS* planes lying on {102} planes. (b) The same fragment after being heated in the electron beam. The {102} *CS* planes have increased in density, and a number have broken into segments with an orientation along {103}. Note especially *CS* plane labeled A, and the *CS* plane segment arrowed.

of the *CS* planes with $m > 4$ is lower than that of {104} *CS* planes, and as the elastic strain energy $(U_s)_2$ is also lower, the transition {104} → {105} → {106} → ... {001} will give out energy. In this case, the {104} *CS* planes should transform directly to {001} and arrays of *CS* planes with $m > 4$ should not be observed. More generally, we expect transitions {102} → {103} →... {$10m_{\max}$} and then {$10m_{\max}$} → {001}, with $m_{\max}$ being probably equal to 4. This is good agreement with the data available to date in both the binary and ternary *CS* phases.

Whether transformations of one *CS* plane type to another are actually observed will depend upon the mechanism of formation of the *CS* plane arrays. In general at the preparation temperatures used (~ 1600°K in the Nb–W–O system for example) the crystals of *CS* phases form by way of a vapor phase mechanism and the initial formation of {102} *CS* planes followed by {103} would not be expected. The change is most likely to be observed in large crystals of WO_3 reduced at rather low temperatures. Such conditions can be achieved in the electron microscope, and if crystals containing ordered arrays of {102} *CS* planes are gently reduced by electron beam heating a partial transformation of {102} to {103} *CS* planes can take place. Figure 5 shows this process.

The changes shown in this figure are worthy of some comment. First one can note that rather small regions of *CS* plane rotate and that at low magnifications the *CS* planes take on a wavy appearance. This has the advantage, as Anderson has pointed out (*15*), of permitting readily reversible behavior in the regions where *CS* planes swing from one orientation to another. The internal energy is raised, though, by the extra lattice strain in the region of terminating *CS* planes, and there is no doubt that prolonged annealing would cause the *CS* planes to reorganize themselves into linear arrays. This process, however, is likely to be relatively slow.

Stability of homologs

Within any one family of *CS* planes it has been found empirically that some homologs, those with n even in the W_nO_{3n-1} series based upon ordered {102} *CS* planes for example, are favored over those with n odd. Similar behavior is found in other *CS* phases, including rutile based structures (see, e.g., (*16*)) and this has led to the supposition that some members of a series are thermodynamically more stable than others. The formation energy of the *CS* planes should not play a controlling role in this, only the interaction forces, so we should be able to analyze the situation using the $(U_s)_2$ data in Fig. 3. Such an analysis had already been described for {102}, {103} *CS* phases (*9*).

Let us consider here the case of {104} *CS* phases. In general a preparation will be made by heating reactants in a sealed tube. We suppose that the composition is such as to form the oxide W_nO_{3n-3} where we ignore the presence of ternary metal dopants. We can imagine that either this oxide will form, or else it will gain in energy by disproportionating to its neighboring homologs W_qO_{3q-3} $(q = n - 1)$ and W_pO_{3p-3} $(p = n + 1)$. If we assume that the driving force for this is $(U_s)_2$ we can readily calculate whether we will achieve a gain or a loss of energy (*9*), and we can generally state that if

$$(U_s)_2^n > \tfrac{1}{2}[(U_s)_2^q + (U_s)_2^p]$$

we get disproportionation, while if

$$(U_s)_2^n < \tfrac{1}{2}[(U_s)_2^p + (U_s)_2^p]$$

we will not get disproportionation. In Table I we have shown values of $\Delta(U_s)_{n'}^n = (U_s)_2^n - \tfrac{1}{2}[(U_s)_2^q + (U_s)_2^q]$ for {104} *CS* phases. If $\Delta(U_s)_{n'}^n$ is positive the phase will disproportionate to the phases on either side while if $\Delta(U_s)_{n'}^n$ is negative the W_nO_{3n-3} oxide will be stable. The results in Table I show an irregular sequence, and reveal that in any preparation oxide phases with compositions close to the starting composition will be found. This is in agreement with results in the $Nb_2O_5 \cdot WO_3$ system, where {104} *CS* planes form, as there is no evidence of disproportionation and n values in the range of 54–63 have been observed (*17*, *18*).

These calculations can readily be extended to other {10m} *CS* plane series. However, little experimental evidence is available except for the {001} arrays in NbO_2F and the niobium-doped tungsten oxides. In the case of NbO_2F reduction leads to Nb_3O_7F, the member of the homologous series $M_n(O,X)_{3n-1}$ with $n = 3$ (*7*). Calculations for {001} which parallel those above for {104} *CS* planes have been reported earlier (*9*). In these it was found that disproportionation is favored, and in terms of elastic strain energy alone, the parent matrix containing a very low density of *CS* planes in which $(U_s)_2$ is effectively zero, should coexist with a phase in which n is 8, or lower. All higher n values would tend to disproportionate into these two end members. Taking into account the fact that many other terms in

TABLE I

THE STABILITY OF VARIOUS MEMBERS OF THE HOMOLOGOUS SERIES OF OXIDES W_nO_{3n-3}, CONTAINING ORDERED ARRAYS OF {104} *CS* PLANES

n	Formula, W_nO_{3n-3}	$(U_s)_2{}^a$	$\Delta(U_s)^{n\,a}_{n'}$	Stability[b]
13	$W_{13}O_{36}$	0.169088		
14	$W_{14}O_{39}$	0.157600	−0.007694	S
15	$W_{15}O_{42}$	0.161500	−0.011744	S
16	$W_{16}O_{45}$	0.188888	+0.013530	U
17	$W_{17}O_{48}$	0.189216	+0.004486	U
18	$W_{18}O_{51}$	0.180572	−0.008952	S
19	$W_{19}O_{54}$	0.189832	+0.004916	U
20	$W_{20}O_{57}$	0.189260	−0.012261	S
21	$W_{21}O_{60}$	0.213210	+0.015389	U
22	$W_{22}O_{63}$	0.206382	−0.006759	S
23	$W_{23}O_{66}$	0.213072	−0.002433	S
24	$W_{24}O_{69}$	0.224628	+0.008418	U
25	$W_{25}O_{72}$	0.219346	−0.001434	S
26	$W_{26}O_{75}$	0.216936	−0.010078	S
27	$W_{27}O_{78}$	0.234680	+0.011333	U
28	$W_{28}O_{81}$	0.229754	−0.002318	S
29	$W_{29}O_{84}$	0.229464	+0.000098	U
30	$W_{30}O_{87}$	0.228978	−0.001698	S
31	$W_{31}O_{90}$	0.231888	−0.000475	S
32	$W_{32}O_{93}$	0.235748	+0.001194	U
33	$W_{33}O_{96}$	0.237220	+0.000503	U
34	$W_{34}O_{99}$	0.237686	+0.000238	U
35	$W_{35}O_{102}$	0.237676	−0.002316	S
36	$W_{36}O_{105}$	0.242298	+0.001432	U
37	$W_{37}O_{108}$	0.244056	−0.000552	S
38	$W_{38}O_{111}$	0.246918	+0.001928	U
39	$W_{39}O_{114}$	0.245924	−0.001346	S
40	$W_{40}O_{117}$	0.247622	−0.000148	S
41	$W_{41}O_{120}$	0.249616	−0.000003	S
42	$W_{42}O_{123}$	0.251616	+0.000697	U
43	$W_{43}O_{126}$	0.252222	−0.000128	S
44	$W_{44}O_{129}$	0.253084	−0.000292	S
45	$W_{45}O_{132}$	0.254530	+0.000043	U
46	$W_{46}O_{135}$	0.255890	+0.000163	U
47	$W_{47}O_{138}$	0.256924	+0.000189	U
48	$W_{48}O_{141}$	0.257580	−0.000156	S
49	$W_{49}O_{144}$	0.258548	−0.000056	S
50	$W_{50}O_{147}$	0.259628	+0.000109	U
51	$W_{51}O_{151}$	0.260490	+0.000021	U
52	$W_{52}O_{154}$	0.261310	+0.000126	U
53	$W_{53}O_{157}$	0.261878	−0.000084	S
54	$W_{54}O_{160}$	0.262614	−0.000024	S
55	$W_{55}O_{163}$	0.263398	+0.000073	U
56	$W_{56}O_{166}$	0.264036	−0.000263	S
57	$W_{57}O_{169}$	0.265200	+0.000635	U
58	$W_{58}O_{172}$	0.265094		

[a] The units of $(U_s)_2$ and $\Delta(U_s)^n_{n'}$ are (C/a^2).

[b] S = stable; U = unstable.

addition to $(U_s)_2$ are of importance in controlling crystal structures, this is in fair agreement with the experimental findings for NbO_2F. {001} *CS* plane arrays also form in the $Nb_2O_5 \cdot WO_3$ system (*17*). In this case the analysis is complicated by the fact that {104} and {103} *CS* planes also form. However, our own results (*18*) suggest that the true equilibrium situation consists of a mixture of slightly reduced WO_3 containing a few {102} *CS* planes and crystals containing arrays of {001} *CS* planes with n values in the range 8–14, but centered upon $n = 10$. This lies on the other side of the theoretical result from NbO_2F, and suggests that other factors as well as elastic strain are important, but once again the overall agreement between theory and experiment is fair.

In general, therefore, the assumption that the most stable members of a homologous series are those corresponding to minimum values of the elastic strain energy $(U_s)_2$ seems to hold fairly well. For {102} and {001} arrays the calculations suggest that equilibrium should lie between the almost unreduced parent phase and a homolog with a fairly low n value, in the region of 10. This means that oxide mixtures will generally disproportionate into a greatly reduced component and a component which is only slightly reduced. Experimentally this is found to be so. On the other hand, {103} and {104} *CS* plane series have a large number of stable homologs, suggesting that a preparation will result in phases of overall composition fairly close to that of the starting material. Once again, this behavior is well supported by the experimental evidence. The overall conclusion to be drawn from this is that the elastic strain energy in the matrix between *CS* planes does have a role to play in controlling the microstructures of these materials.

Conclusions

The results described above suggest that elastic strain is an important factor in controlling the microstructures observed in ReO_3-

related *CS* phases. It is also clear, however, that the formation energy of the *CS* planes may outweigh the elastic strain terms, and it is this factor which determines which phases form initially. One would therefore expect that *CS* plane microstructures could well be sensitive both to heating times and heating temperatures during preparation. However, such considerations will need accurate data concerning the mechanism of *CS* formation before the topic can be taken further.

It should also be explicitly stated that although the elastic strain energy seems to be of some importance, it is not the only factor to consider. Bonding, both cation–anion and cation–cation, is likely to be of great importance, and it is certainly true that the chemical nature of the ions involved has a great bearing on the microstructures of the materials. Another factor which may be of importance is the polarization of the crystal, which will be reflected in the observed value of the dielectric constant of the material. Our present results suggest that it is only materials with a high dielectric constant which support *CS* plane formation (*19*). These other factors, in contrast to elastic strain, are extremely difficult to assess quantitatively, but it is hoped that they will form the basis of future studies on the energetics and stability of *CS* phases and related materials.

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