

The Energy of Crystallographic Shear Plane Formation in Reduced Tungsten Trioxide

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The free energy of crystallographic shear (CS) planes in reduced tungsten trioxide has been considered in a semiquantitative fashion. The CS planes are treated as chemical defects in the tungsten trioxide structure and the energy to create such defects is considered to be largely due to enthalpy contributions due to chemical bond breaking. An assessment of this enthalpy term for the various CS plane types known in the tungsten oxide based CS phases is made and the results are then used to explain the experimentally observed CS plane microstructures in binary and ternary tungsten oxide CS phases.

Introduction

When tungsten trioxide is reduced to compositions between approximately WO_3 and $\text{WO}_{2.88}$ the change in anion to cation stoichiometry is accounted for by the formation of crystallographic shear (CS) planes (1-4). If the degree of reduction is small, that is, from WO_3 to approximately $\text{WO}_{2.97}$, the CS planes lie upon {102} planes¹ while if the composition is below about $\text{WO}_{2.93}$ the CS planes are found upon {103} planes. Samples prepared with compositions in the range $\text{WO}_{2.97}$ to $\text{WO}_{2.93}$ are usually mixtures of oxygen-rich crystals containing {102} CS planes and oxygen-poor crystals containing {103} CS planes.

If tungsten trioxide is reduced with small amounts of other metals to yield compounds of overall formula $(M,W)\text{O}_{3-x}$ a variety of structures are formed which include perovskite-related bronzes, tunnel compounds, and CS phases (5). Of these, only the Ti-, Nb-, Ta-, Mo-, and Ge-W-O systems are known to contain CS phases, although many ternary systems still remain to be studied in detail

from this point of view. In the Nb-W-O (6, 7) and Ti-W-O (8) systems, besides {102} and {103} CS planes, {104} and {001} CS planes form as the overall degree of reduction increases. In the case of Ta (7, 9) and Ge (9) only {102} and {103} CS planes are found, but a careful study of the composition range over which they form has not yet been reported. The Mo-W-O oxides (10, 11) appear to contain only {102} CS phases.

Thus, in the tungsten oxides which support oxygen loss by the formation of CS planes there is a definite order of preference with {102} CS planes forming first at lowest degrees of reduction, and then proceeding via {103} and {104}, possibly through higher CS planes {10*m*} to {10 ∞ }, equivalent to {001}.

Despite this knowledge there have been very few attempts to explain these features quantitatively. The question of the stability of CS planes as opposed to point defects has been considered by Anderson and Burch (12) using lattice energy calculations, but no conclusions concerning the WO_{3-x} system were reached. In addition there have been a number of speculative discussions about the nature of the interaction forces between CS planes (13, 14) and one quantitative estimate

¹ These indices refer to an idealized cubic WO_3 cell of the DO_9 (ReO_3) structure type.

of the interaction energy between *CS* planes due to elastic strain in an idealized ReO_3 matrix (15).

These papers do not consider at all the question of why the sequence of *CS* planes described above is always adhered to, or why in some of the systems only {102} and {103} *CS* planes are formed while in the others higher *CS* planes families also occur. These questions are considered in a semiquantitative way in this paper, while a future communication will give the results of detailed quantitative calculations of the interreaction energies between these families of *CS* phases.

Structural Considerations

The essential features of the geometry of the *CS* planes mentioned in the introduction have been described by Magnéli (16), Allpress (6), and Bursill and Hyde (7). The most important features are summarized here. Figure 1 shows the idealized structures of various {10*m*} *CS* planes. They are composed of blocks of edge-sharing octahedra set in a matrix of corner-sharing octahedra which is characteristic of the idealized WO_3 structure. They can be made formally by collapse of the parent WO_3 lattice along the appropriate {10*m*} plane. In this process oxygen is eliminated from the lattice and the oxygen to metal stoichiometry changes (17). It is a fairly straightforward process to show that one oxygen atom is lost in forming the block of four edge-sharing octahedra characteristic of a {102} *CS* plane, two are lost in the block of six edge-sharing octahedra in a {103} *CS* plane, and in general (*m* - 1) are lost in a {10*m*} *CS*

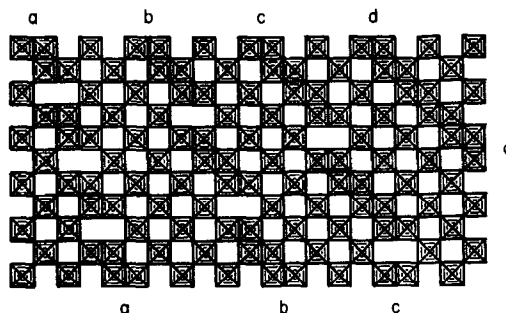


FIG. 1. The idealized structures of some {10*m*} *CS* planes in WO_3 ; (a) {102}, (b) {103}, (c) {104}, (d) {001}. The shaded squares represent metal-oxygen octahedra.

plane. If the {10*m*} *CS* planes form an ordered array in an $(M,W)O_{3-x}$ crystal, the oxide so produced can be considered to be a member of a homologous series of oxides $(M,W)_nO_{3n-(m-1)}$. As the spacing between *CS* planes changes, so does the formula of the oxide and the stoichiometry of the crystal. These relationships between *CS* plane geometry and stoichiometry are included in Tables I and II.

Although the real structures of the *CS* planes shown in Fig. 1 are not known, they will, in general, be made up of somewhat distorted metal-oxygen octahedra rather than idealized ones. These distortions would be expected to change both with temperature and the distance between neighboring *CS* planes. The microstructures of crystals containing *CS* planes are usually complex, with *CS* planes often found on several of the possible {10*m*} planes, and spacings between *CS* planes usually spread over a wide range of values. As these microstructures are not central to the

TABLE I
RELATION BETWEEN *CS* PLANE GEOMETRY AND CRYSTAL STOICHIOMETRY

<i>CS</i> plane indices	Formula of series	<i>CS</i> plane spacing, <i>d</i>	Data for composition $MO_{2.90}$
{102}	M_nO_{3n-1}	$(n - \frac{1}{2})a/5^\ddagger$	$n = 10; d = 1.614 \text{ nm}$
{103}	M_nO_{3n-2}	$(n - 1)a/(10)^\ddagger$	$n = 20; d = 2.283 \text{ nm}$
{104}	M_nO_{3n-3}	$(n - \frac{3}{2})a/(17)^\ddagger$	$n = 30; d = 2.627 \text{ nm}$
{10 <i>m</i> }	$M_nO_{3n-(m-1)}$	$(n - (m - 1/2)a/(m^2 + 1)^\ddagger$	$n = 10(m - 1); d = \frac{19(m - 1)a}{2(m^2 + 1)^\ddagger}$
{001}	M_nO_{3n-1}	$(n - \frac{1}{2})a$	$n = 10; d = 3.610 \text{ nm}$

TABLE II^a

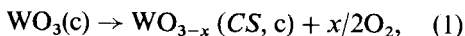
CS plane indices	Length of repeat unit	Number of O atoms lost per unit	Bonding energy change
102	$\sqrt{(5a)}^\ddagger$	1	0.8944C
103	$\sqrt{(10a)}^\ddagger$	2	1.2649C
104	$\sqrt{(17a)}^\ddagger$	3	1.4552C
105	$\sqrt{(26a)}^\ddagger$	4	1.5689C
10 <i>m</i>	$(m^2 + 1)^\ddagger a$	$m - 1$	$(m - 1)C/2(m^2 + 1)^\ddagger$
001	a	1	2.0000C

^a C is a constant equal to $(\Delta H/a)$, where ΔH is the net enthalpy change involved in the loss of one oxygen atom from the crystal and a is the length of the diagonal of a (WO_6) octahedron, approximately 0.38 nm.

theme of this paper they are not considered in detail here, but have been illustrated in a number of prior publications (6-8, 18-22).

Thermodynamic Considerations

We have attempted to account for the sequence of CS planes observed in these oxides by an estimate of some of the principle terms expected in the free energy function of a crystal containing CS planes. To do this, we have considered that the overall reaction taking place is of the form



where WO_3 crystals are reduced to WO_{3-x} crystals containing CS planes. As observation on such crystals shows them to contain disordered or at best only imperfectly ordered arrays of CS planes (6-8, 18-22), we can consider these systems as being made up of perfect WO_3 containing variable numbers of CS planes, which can be regarded as chemical defects (23). In this way we can treat the CS populations by methods somewhat analogous to those used in the past to elucidate point defect behavior in non-stoichiometric solids. To this end we can follow the general procedure described by Anderson (24) and so write the

free energy, G , of an $(M,W)\text{O}_{3-x}$ crystal containing N_d CS planes as

$$G(N, N_d, T) = G_0(N) + G_d(N, N_d) + G_i(N_d), \quad (2)$$

where N is the number of atoms in the crystal, and the free energy has been subdivided into three parts, G_0 , the free energy of the perfect WO_3 crystal before reduction, G_d , the free energy of the N_d noninteracting CS planes and G_i , which contains terms due to the interactions between the CS planes with the surrounding WO_3 matrix and with each other.

In the main, we can consider the first term, G_0 , to control the overall phase equilibrium and $G_d + G_i$ to be of the nature of a small perturbation. For example, a knowledge of G_0 and the partial pressure of oxygen over the crystals will reveal whether WO_3 or one of the lower phases $\text{W}_{18}\text{O}_{49}$, WO_2 , or W metal will be stable.

As thermodynamic data are available for two CS phases, $\text{WO}_{2.96}$ and $\text{WO}_{2.90}$ (25-27), it is possible to make a comparison of the magnitudes of G_0 and $G_d + G_i$. As the oxide $\text{WO}_{2.90}$ ($\text{W}_{20}\text{O}_{58}$, a {103} CS phase with $n = 20$) has been most frequently examined we can use this as an example. The free energy of formation of WO_3 and $\text{WO}_{2.90}$ per gram atom of tungsten at 1000°K, taken from the data of Rizzo, Bidwell, and Frank (26) are

$$\Delta G_f^0(\text{WO}_3, \text{c}) = -588.88 \text{ kJ mole}^{-1} \equiv G_0$$

$$\begin{aligned} \Delta G_f^0(\text{WO}_{2.90}, \text{c}) &= -572.26 \text{ kJ mole}^{-1} \\ &\equiv G_0 + G_d + G_i. \end{aligned}$$

We can then estimate within this approximation that

$$\begin{aligned} G_d + G_i(\text{WO}_{2.90}) &= \Delta G_f^0(\text{WO}_3) \\ &\quad - \Delta G_f^0(\text{WO}_{2.90}) \\ &= +16.62 \text{ kJ mole}^{-1}. \end{aligned}$$

In general, one would expect the final term, G_i , to be small when very few CS planes are present, but that it would become increasingly important as the CS plane concentration rises. For the purposes of explaining why the initial reduction of WO_3 leads to the formation of isolated {102} CS planes we can therefore

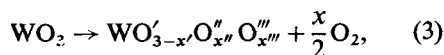
put G_i to one side and attempt to estimate the relative values of G_d for the CS plane types known to occur.

The formation of a CS plane can be formally represented by two steps, the abstraction of a plane of oxygen atoms followed by collapse (17). The free energy term G_d will therefore be composed of the following major component: U_i , the "lattice energy" of the strip of edge-sharing octahedra forming the CS plane itself, U_s , the elastic strain energy of these octahedra; a pV work term, due to the collapse process, a vibrational and configurational entropy term, S , an interfacial term, σ_s , due to the fact that the CS plane forms an internal interface within the crystal, and an energy term due to the rupture of $W-O$ bonds during the oxygen loss step.

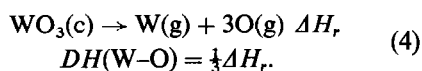
While it is difficult to make estimates of the absolute values of each of these terms, it seems reasonable to consider that the bond breaking process will be dominant. For instance, strain energies, interfacial energies and terms relating to the pV (work) terms are much less important than chemical (bond) energies in most chemical reactions and are often neglected in thermodynamic evaluations. Similarly, the entropy contribution would not be expected to dominate the terms above, which are effectively enthalpy terms, although entropy considerations may play an important part in influencing the real microstructure of a crystal containing $\{10m\}$ CS planes. In this approximation then, we can consider G_d to be dominated by loss of oxygen from the crystal and the bonding energy changes involved in this process.

It is possible to estimate this energy and see if the magnitude does agree with the available thermodynamic data. We can illustrate this by reference again to $WO_{2.90}$. As described in the previous section, the formation of each of the blocks of six edge-sharing octahedra characterizing a $\{103\}$ CS plane involves the loss of two oxygen atoms. We can consider this from an idealized standpoint. Firstly, the loss of two oxygen atoms will involve the breaking of two (i.e., four halves) $W-O$ bonds in the crystal. Secondly, the two oxygen atoms will unite to form a molecule of oxygen. In reality, the process will be far more

involved than this, as WO_3 does not lose oxygen gas when heated under vacuum, but more complex tungsten-oxygen species. In addition, the types of oxygen in the residual crystal containing CS planes can be separated into several species, oxygen in the WO_3 matrix between the CS planes, and two sorts of oxygen in the CS plane block of six octahedra. In this case, one could write a more accurate equation representing the micro-process as



where $x' + x'' + x''' \equiv x$ in Eq. (1). Similarly, we may need to distinguish tungsten atoms in the CS plane and in the bulk. Also, one can note that the bond energy terms for the oxygen abstraction will be compensated for when the crystal "collapses" to form a CS plane. Nevertheless, it is possible to obtain a reasonable working estimate of the energy change involved to compare with the thermodynamic data already cited even if we ignore these complications. We can say, therefore, that the overall enthalpy change in the formation of a unit of $\{103\}$ CS plane will be given by the energy required to break two $W-O$ bonds minus the energy released in forming one molecule of O_2 from oxygen atoms. We can define the average bond energy of the tungsten-oxygen bond in WO_3 by one-third of the enthalpy of reaction (4), viz.,



Using the following values for the enthalpies of formation of the various components of Eq. (4); $\Delta H_f^0(WO_3, c) = 843.11 \text{ kJ mole}^{-1}$, $\Delta H_f^0(W, g) = 851.23 \text{ kJ mole}^{-1}$, $\Delta H_f^0(O, g) = 242.2 \text{ kJ mole}^{-1}$ (28) and choosing the chemical potential of molecular oxygen as the standard state we find that the $W-O$ bond energy, $DH(W-O) = 244.91 \text{ kJ mole}^{-1}$. The enthalpy per bond is then readily obtained by dividing by Avogadro's number, N . The energy released when the oxygen atoms reunite is also simply given by $2\Delta H_f^0(O, g) = 484.4 \text{ kJ mole}^{-1}$, which is also divided by N to yield the energy per pair of oxygen atoms released during the reduction.

In order to complete the calculation it is necessary to know how many blocks of six edge-sharing octahedra there are in 1 mole of $\text{WO}_{2.90}$. To do this we must arbitrarily assign a shape and size to the crystal containing CS planes. In practice this is not a severe limitation, as the *area* of CS plane per mole of WO_{3-x} generated is not so dependent upon crystal habit although the number of CS planes in the crystal is. For convenience, we have chosen a crystal of rectangular habit containing N unit cells of "cubic" WO_3 , each of side a , and with sides $N^{\frac{1}{3}}a$ along [010], $((10)^{\frac{1}{3}}/3)N^{\frac{1}{3}}a$ along [103] and $(3/(10)^{\frac{1}{3}})N^{\frac{1}{3}}a$ along [301]. The number of {103} CS planes which are needed to reduce the composition from WO_3 to $\text{WO}_{2.90}$ is given by dividing the length of the side normal to the CS planes, i.e., along [301], by the CS plane separation, 2.33 nm for $\text{W}_{20}\text{O}_{58}$ ($\text{WO}_{2.90}$), to yield $(3/(10)^{\frac{1}{3}})N^{\frac{1}{3}}a/2.33$. The total CS plane area is then obtained by multiplying by $[((10)^{\frac{1}{3}}/3)N^{\frac{1}{3}}a \times N^{\frac{1}{3}}a]$ to give $(Na^3/2.33)$ nm² mole⁻¹. The total number of blocks of six edge-sharing octahedra is found by dividing by the area of each block, $(10)^{\frac{1}{3}}a^2$, to give a final value for the number of such blocks as $(Na/(10)^{\frac{1}{3}}2.33)$ mole⁻¹. This value is only an estimate, and in practice much will depend upon crystal habit and exact stoichiometry, but it will suffice for the present purposes.

The total enthalpy change per mole of $\text{WO}_{2.90}$ can now be estimated by multiplying the total number of blocks of six edge-sharing octahedra by the net enthalpy change per block calculated from the data above, i.e.,

$$\begin{aligned} \Delta H(103) &= \left[\frac{2(484.4) - 2(244.91)}{N} \right] \frac{Na}{(10)^{\frac{1}{3}} 2.33} \\ &= 24.70 \text{ kJ mole}^{-1}. \end{aligned} \quad (5)$$

We can compare this with the experimentally determined enthalpy change. For this purpose, the most recent data are those of Charlu and Kleppa (27) who quote $\Delta H_f^0(\text{WO}_{2.90}, c)$ as 816.21 kJ mole⁻¹. $\Delta H_f^0(\text{WO}_3, c) - \Delta H_f^0(\text{WO}_{2.90}, c)$ is then found to be 26.90 kJ mole⁻¹, which is in good agreement with the estimated value using bond energies alone. It would therefore seem that the assumption that bonding energy changes are dominant in the

reaction is reasonably well justified, as the higher experimental value will also contain interaction terms neglected here.

We are now in a position to estimate the relative enthalpies of formation of all of the CS planes described earlier. If we assume that the net enthalpy change due to chemical bonding for the loss of one oxygen atom is ΔH , which we have estimated to be about 4×10^{19} J from the data in Eq. (5), we can readily write down the relative enthalpies per unit length for the other {10*m*} CS planes. These values are listed in Table II. The differences between successive pairs of CS planes are most significant at the {102} end of the series, the ratio of values being 1.4 for {103}:{102}. It would then seem reasonable to conclude that the formation of {102} CS planes is preferred over all others because of this lower formation energy per unit length and that we will then find, in order of preference {103}, {104} . . . {001}.

Thus, at low degrees of reduction of WO_3 , we will expect {102} CS planes to nucleate at random in the crystals, increasing the free energy of the crystal of G_d per CS plane. However, as the CS plane density increases the interaction between the CS planes will increase, causing the G_i term to become more and more important, as shown in Fig. 2. It should be noted that the resulting G versus composition curve can be more precisely regarded as the envelope of the minima of a

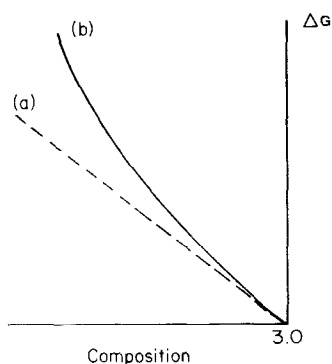


FIG. 2. Schematic representation of the components of the free energy of a reduced tungsten trioxide crystal containing {102} CS planes with composition. (a) refers to the contribution of the term G_d alone and (b) to $G_d + G_i$. (See text for details).

closely spaced succession of sharp free energy blades, each corresponding to a different CS phase in the way described by Anderson (24). This particular aspect is not, though, of central importance here, and for the purposes of our discussion we can regard the G versus composition function to be continuous. Hence, as the degree of reduction increases, a point will be reached where the total excess free energy for the {102} CS plane array will become higher than that of an array of {103} CS planes which yields the same degree of reduction. This is because fewer {103} CS planes are needed to reach the composition WO_{3-x} than {102} CS planes as shown in Table I, and therefore although the G_a term for {103} CS planes is higher, the G_t term at this particular composition will be lower. Experimentally, it would seem that this change occurs at values of about $W_{12}O_{3.5}$ for {102} CS phases. These changes in $(G_a + G_t)$ with composition are shown schematically in Fig. 3.

Clearly, the process can be imagined to continue. At a critical composition WO_{3-x} corresponding to a {103} CS phase W_nO_{3n-2} , the interaction energy between CS planes will become large enough to make the change to a {104} CS phase W_nO_{3n-3} , with correspondingly fewer CS planes for the same degree of reduction WO_{3-x} , an energetically favorable

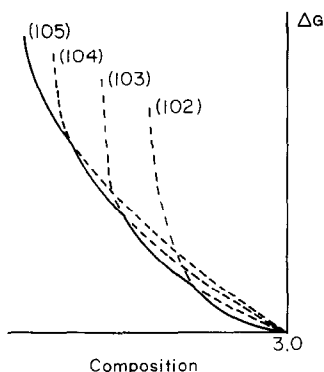


FIG. 3. Schematic representation of the free energy of a reduced tungsten trioxide crystal containing, as the composition falls, CS planes successively on, {102}, {103}, {104}, and {105} planes. The dotted parts of each curve correspond to nonobserved or metastable phases.

one. The crystal will then accommodate oxygen loss on {104} CS planes until they too approach each other closely and the G_t term becomes prohibitive, when the transformation to {105} will take place. Ultimately, we will end with {001} CS planes

Discussion

In the previous section we have suggested that {102} CS planes have the lowest effective formation energy and hence will be nucleated in preference to other CS planes if the interaction term, G_t , is low. This is supported by electron microscope observation of the growth of CS planes in thin crystal flakes due to electron beam heating. In slightly reduced crystals containing few {102} CS planes, only {102} CS planes form in this way on reduction, and other CS plane types have never been seen to nucleate or grow (19, 22, 29). In crystals containing {103} and {001} CS planes, the type of CS plane formed depends, as one would anticipate, upon the spacing of the CS planes. If these are close together, the new CS plane will grow parallel to the existing family (29, 30). However, when the spacing between the CS planes is further apart, the CS plane forms upon a {102} plane. It then grows until it is close enough to its neighbors for the interaction energy to become significantly high, at which stage it will either stop growing, or else be deflected into an orientation parallel to the original set. An example of this is shown in Fig. 4, for CS plane growth in a predominantly {103} family of CS planes in a WO_3 crystal doped with Ti. Further details of CS plane growth due to the influence of electron beam heating during electron microscope observation are to be found elsewhere (19, 22, 29, 30).

After the introduction of the initial {102} CS planes, the sequence of CS phases then formed will depend upon how far along the composite set of free energy curves shown in Fig. 3 the crystal progresses. At any particular gross sample composition, therefore, the phases present in the system will be obtained by use of the "tangent rule" normally employed in multicomponent reactions.

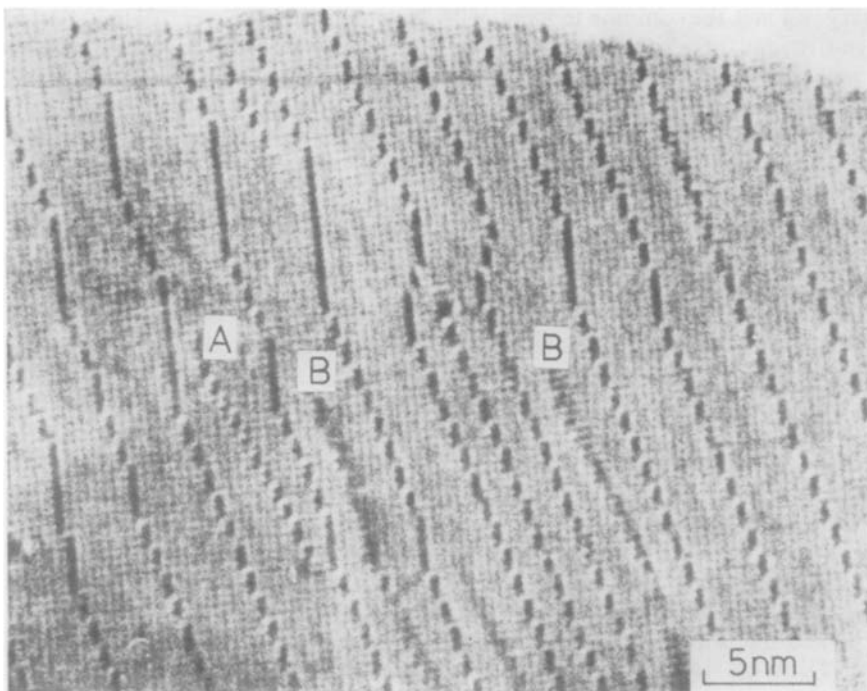


FIG. 4. Electron micrograph of a crystal fragment from an oxide of approximate composition $\text{Ti}_{0.01}\text{W}_{0.99}\text{O}_{2.90}$ containing mostly $\{103\}$ CS planes. The CS plane A grew in the electron beam and lies on $\{102\}$. The dark lines B are disordered regions where other $\{102\}$ CS planes are forming.

In the present case, as we proceed to reduce the overall composition of the sample from WO_3 , the common tangent of each successive "phase" will be the envelope of the sharp G vs composition blades described earlier, and that is simply the curve shown in Fig. 3. At some stage when the interaction terms start to become important, the common tangent will start to intersect the $\{103\}$ CS plane curve and at this point the most stable reaction product will be a "two-phase" mixture of relatively slightly reduced WO_{3-x} containing $\{102\}$ CS planes and more substantially reduced crystals containing $\{103\}$ CS planes (Fig. 5). Compositions intermediate to these two points will then be unstable and will disproportionate into a mixture of $\{102\}$ and $\{103\}$ CS planes in separate crystals. Experimental evidence suggests that in the binary W-O system samples with compositions between approximately $\text{WO}_{2.93}$ and $\text{WO}_{2.97}$

disproportionate into $\sim\text{WO}_{2.97}$ containing $\{102\}$ CS planes and $\sim\text{WO}_{2.93}$ containing $\{103\}$ CS planes.

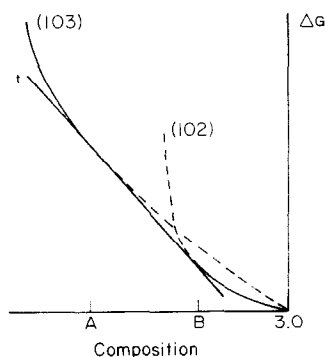


FIG. 5. The common tangent, t , joining the curves representing the free energy of $\{102\}$ and $\{103\}$ CS planes. Samples with compositions lying between the points A and B will consist of mixtures of the two phases with compositions A and B.

In ternary systems, the common tangent will not necessarily join these same two compositions. If, in a particular ternary system the G_t term is small, then the {102} *CS* family would be expected to persist to much lower n values than in the binary W–O system. Such a situation appears to occur in the ternary (Mo, W)– O_{3-x} oxides (10, 11). In a similar way, if the interaction term G_t is larger than in the binary system the change to {103} *CS* planes will come sooner. If this case the {103} series will seem to be “stabilized” to higher n values than in the binary W–O system. This seems to hold for the ternary (Ta, W) O_{3-x} oxides (7, 9).

Further reduction of the crystals will follow the {103} envelope, effectively allowing a continuous variation in composition change, until the interaction terms start to increase the value of the free energy significantly and enable the tangent to be drawn between the {103} curve and the next lowest curve. In the case of Nb_2O_5 – WO_3 this is to the {104} set. However, in the binary system, it appears that a lower free energy is obtained by drawing the tangent to $W_{18}O_{49}$ or to the $WO_{2.82}$ phase recently reported (31), and the lowest {103} *CS* phase formed seems to be close to $W_{16}O_{30}$. It is clear, therefore, that the sequence of *CS* phases {102}, {103}, . . . {10*m*} . . . {001} will terminate when the common tangent has one end located on a non-*CS* structure. Thus, one would expect different situations to arise when considering the various composition lines in phase diagrams. For example, the behavior along the MO_2 – WO_3 , M_2O_5 – WO_3 , and M_xWO_3 lines will then depend upon the various neighboring non-*CS* equilibrium phases formed and their free energies relative to the *CS* phases. Thus we can, in a general way, understand why no *CS* phase formation takes place in the TiO_2 – WO_3 pseudobinary system, why {104} and {001} *CS* phases form in the Nb_2O_5 – WO_3 system before giving way to tetragonal tungsten bronze structures (6, 32), and why the Ta_2O_5 – WO_3 system only forms {103} *CS* phases before the tetragonal tungsten bronze type of phases become preferred. As high temperatures will affect all the free energy functions substantially, it is also possible to understand why a *CS* phase field

may exist only over a limited temperature range, as well as composition range, as is found in the Nb_2O_5 – WO_3 oxides (6, 32).

As with other related phase changes, it is possible to imagine that metastable phases will also form in the *CS* phases under certain conditions. The most obvious of these is if we consider the reduction process in a large crystal where solid-state reaction is taking place rather than the more usual preparation methods using powders, where extensive vapor phase reaction ensures a fairly good approach to equilibrium structures. If we follow the path of reduction of a large crystal, nucleation of new *CS* planes will involve the formation of {102} *CS* planes because of their lower formation energy per unit length. When the composition of approximately $WO_{2.97}$ is reached the system will gain energy by formation of {103} *CS* planes. This, however, will involve considerable solid-state rearrangements. In practice, therefore, it is quite easy to produce fairly well ordered {102} *CS* phases in the binary W–O system with compositions down to $W_{12}O_{23}$ simply by working with fairly large crystals and rather lower temperatures (21).

A similar apparently nonequilibrium situation is found when WO_{3-x} crystals containing {103} *CS* planes are observed electron microscopically. Often, under the conditions employed for observation, the crystals lose oxygen, as mentioned earlier. If these latter have a spacing corresponding approximately to oxides $W_{22}O_{64}$ or higher n , new *CS* planes nucleate between them to yield an oxide of approximate formula $W_{12}O_{34}$ (29, 30), although such oxides are not normally formed in experiments using powdered reactants, where $W_{18}O_{49}$ forms instead. It is likely that the careful reduction of single crystals of these higher n {103} *CS* phases outside the electron microscope in conditions avoiding vapor phase reaction would yield similar metastable crystals, analogous to the {102} *CS* phases.

Because of the assumptions and simplifications made in this discussion of *CS* plane energies, the considerations presented above are perhaps best regarded as a guide to the expected course of reduction of WO_3 crystals under somewhat idealized conditions. In

actual fact the sequence of CS phases found will depend on a variety of factors, and in real systems we need to superimpose upon the general trend described here other factors which may modify the overall pattern of microstructures. In this context we can note that in ternary oxides complications arise due to the diffusion of the dopant cations throughout the bulk of the crystal. Cation concentration gradients will cause changes in stoichiometry and may lead to local regions of quite different stoichiometry from that in the major part of the crystal and hence to microstructures far removed from those obtaining at true equilibrium. In addition, it is possible that some cations will have a preference for sites in or near the CS planes and this in turn may favor the development of particular microstructures at the expense of others.

This factor will be a direct consequence of the binding of the ternary ions in the structure, and will depend critically upon cation-cation and cation-anion-cation orbital interactions. As such, these interactions may alter the real value of G_0 in Eq. (2) as well as G_d and G_t and a far more complex analysis of the situation is needed to take such matters into account. Such an analysis is hampered by the lack of real knowledge of the microstructures of these ternary systems, and more experimental evidence is needed, particularly in the Nb-W-O, Ta-W-O, and Ti-W-O systems, before a sound basis of experimental fact is available. A more thorough examination of these features, therefore, is best made in conjunction with more detailed observations of the microstructures concerned and will be taken further in future communications.

For similar reasons we will postpone a discussion of CS planes with indices intermediate between $\{102\}$ and $\{103\}$, $\{205\}$ for example, and between the other families of $(10m)$ CS phases discussed above. Such CS planes have not been observed in the tungsten oxides, although it would seem possible that a correct combination of preparation conditions and choice of ternary metal ion M might result in the formation of such families.

In conclusion, one can state that a simple model of CS plane energetics in which the bonding energy of oxygen in the WO_{3-x}

crystal is considered to dominate CS plane formation at low degrees of reduction and CS plane interactions become significant at high CS plane densities accounts well for the observed CS plane structures in $(M, W)O_{3-x}$ crystals. In order to investigate the microstructures in more detail, the interaction forces between CS planes must be known. These have been calculated quantitatively and will be presented in a future communication.

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