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The Elastic Strain Energy of Crystallographic Shear Planes in ReO_3-Related Oxides. I. The Formation Energy of Isolated *CS* Planes

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The formation energy of isolated *CS* planes in the ReO_3 structure type has been estimated. The *CS* planes considered are {102}, {103}, {104}, {105}, {106}, {107}, and {001}. The major components of the formation energy were considered to be the loss of oxygen from the crystal and the elastic strain energy of the matrix surrounding the *CS* plane so formed. In addition, the internal energy of the *CS* plane itself was also large and of importance. It was found that {102} *CS* planes have the lowest formation energy, but {001} *CS* planes are only slightly less favorable. These results are compared with the experimental data available for the materials NbO_2F and WO_3.

Introduction

There are two materials which possess structures closely related to the ReO_3 (DO_9) type which, on reduction, are known to accommodate the stoichiometry change involved by the introduction of crystallographic shear (*CS*) planes into the parent matrix. The niobium oxyfluoride NbO_2F, which has an undistorted ReO_3 structure, makes use of *CS* planes lying on random {001} planes and substantial reduction leads to the formation of the *CS* phase Nb_3O_7F, which contains ordered arrays of {001} *CS* planes (see (*1–4*) and references therein).

If the oxygen to metal stoichiometry of tungsten trioxide, WO_3, is lowered from 3.0 either by reduction or by doping with the metals Ti, Nb, Ta, or Mo, a variety of crystallographic shear (*CS*) phases form. In these compounds the *CS* planes may take the indices {102},[1] {103}, {104}, or {001} depending upon the degree of reduction, the temperature and the cations involved (*1–4*). Despite the complexity of these systems the experimental evidence available at the present time indicates that {102} *CS* planes are always formed upon initial reduction, regardless of what other *CS* plane types may be preferred at greater degrees of reduction. This fact suggests that the formation energy of {102} *CS* planes in WO_{3-x} is lower than any of the other observed {10*m*} types.

In an attempt to account for this latter observation, Tilley (*5*) discussed the formation energy of *CS* planes in WO_{3-x} semiquantitatively. In this, it was suggested that the energy required to remove oxygen from the WO_3 crystals was important, and if this term dominated the formation energy, then the formation energy per unit length of {102} *CS* planes was lower than the formation energy of

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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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any of the other {10*m*} *CS* planes. It was also pointed out, though, that the free energy of a crystal containing *CS* planes would be dependent upon a number of other energy terms, which were not evaluated. Among these, elastic strain energy and electrostatic interactions are likely to be of some importance.

Recently Iguchi and Tilley (*6*) have calculated the relative elastic strain energies of isolated and ordered arrays of {102}, {103}, and {001} *CS* planes in idealized cubic WO_3 which has the ReO_3 structure and Iguchi (*7*) has succeeded in translating these values into absolute units by investigating the interaction between nonparallel {102} *CS* planes in WO_{3-x}. In addition, the electrostatic interaction energy between isolated {102}, {103}, and {001} *CS* planes and the surrounding crystal matrix in idealized cubic WO_3 and also between pairs of such *CS* planes in the same structure has been evaluated (*8*). These calculations have shown that many aspects of the microstructures of *CS* phases can be explained in a quantitative fashion fairly successfully.

The present paper extends the calculations to a series of {10*m*} *CS* planes in which *m* takes values of from 2 to 7 and ∞. In this first part the results applicable to the formation energy of isolated *CS* planes are reported and are compared with experimental data for the ReO_3-related structures WO_3 and NbO_2F. The second part of the paper (15) considers arrays of *CS* planes in the same compounds.

Structural and Thermodynamic Considerations

The structures of WO_3 and the *CS* phases have been described fully in recent publications (*1–6*) and will only be described briefly here. Tungsten trioxide is composed of an infinite array of corner-linked WO_6 octahedra which are distorted somewhat, but for the purposes of our discussion have been taken as perfect. The resulting structure is of the ReO_3 type, which is also the structure of NbO_2F. The diagonal length of the octahedra in these materials is about 0.38 nm. *CS* planes consist of groups of edge-shared octahedra, aligned along particular {10*m*} planes depending upon the degree of reduction and intergrown within the WO_3 matrix. Figure 1 shows the idealized structures of ReO_3 and some {10*m*} *CS* planes.

In an earlier discussion of the formation energies of *CS* planes (*5*) it was suggested that a reduced WO_{3-x} crystal containing randomly arranged *CS* planes could be regarded as being produced by a reaction of the type

$$WO_3(c) \rightarrow WO_{3-x}(c,CS) + x/2\ O_2 \qquad (1)$$

and if the *CS* planes are considered to be chemical defects, the free energy of the reduced crystal, *G*, could be expressed by the equation

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

where *N* is the number of tungsten atoms in the crystal, G_0 is the free energy of the perfect WO_3 crystal before reduction, G_d is the free energy of the N_d noninteracting *CS* planes, and G_i is the free energy due to all the interactions between the *CS* planes and their surroundings. The same analysis applies to all ReO_3-type crystals, provided that we replace W by the appropriate metal symbol.

In the previous discussion the magnitude of G_i was not estimated and the major contribution to G_d was taken as the energy required to remove oxygen from the crystal. This analysis of the reaction is in many ways too simple to cover all the processes involved in *CS* plane formation, and these will now be considered in more detail, although we still suppose that an equation similar to Eq. (2) will hold, both for binary and ternary *CS* oxides.

Formally the introduction of a {10*m*} *CS* plane into a perfect crystal can be broken up into the following steps.

(i) $(m - 1)$ oxygen vacancies per unit of *CS* plane are introduced into the body of the crystal, where they lie along a single

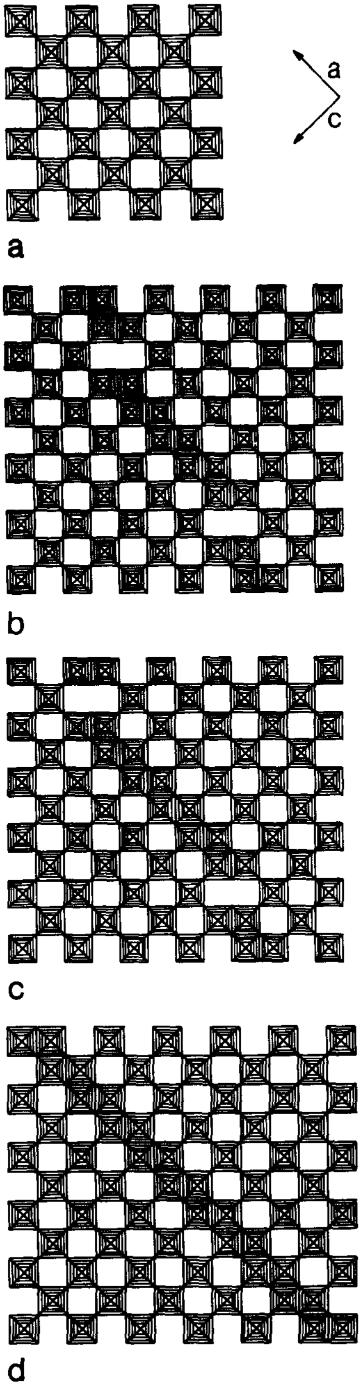

FIG. 1. Idealized representations of (a) the ReO_3 structure which is also the structure of idealized WO_3, (b) a {105} *CS* plane, (c) a {106} *CS* plane, (d) a {001} *CS* plane. The shaded squares represent MO_6 octahedra. The crystallographic *a* and *c* axes are also indicated.

{10*m*} oxygen plane. The internal energy needed to remove this oxygen from the crystal has already been estimated (*5*). We will denote this energy term as U_d.

(ii) After step (i) the crystal collapses along the {10*m*} plane so as to eliminate all the vacancies and to form the *CS* plane. In this process, ions within the newly formed *CS* plane, especially the cations, will now have appreciably greater mutual electronic interactions. We denote the increase in the energy due to these interactions as U_{self}.

(iii) The *CS* plane formed in this way strains the surrounding matrix, and the free energy is further increased by the term, $(U_s)_I$.

(iv) If we assume that each *CS* plane is in a neutral charge state, coulombic interactions between *CS* planes will be zero (*8*). However, even in this case there is an electrostatic interaction between the matrix and an isolated *CS* plane because the charge density in the *CS* plane is higher than in the surrounding WO_3 matrix. This term is denoted by $(U_e)_I$.

(v) Finally, as a *CS* plane can be regarded as a thin lamella of another phase, we may also need to incorporate an interfacial energy term, U_σ, in the equations.

In terms of Eq. (2), U_s, U_σ, and U_{self} are a part of G_d, while $(U_s)_I$ and $(U_e)_I$ are part of G_i. Besides these terms, which are in effect internal energy terms and can reasonably be approximated as enthalpies, entropy terms are needed. Both the configurational and vibrational entropies associated with random arrangements of *CS* planes are difficult to assess (*6*) and in this report will not be considered further.

In addition it is important to remember that the steps outlined above are formal ones only, and not to be supposed to represent the true mechanism of reduction. For example, it is known that the reduction of WO_3 under vacuum is not simply accomplished by the removal of oxygen alone, but that complex tungsten–oxygen molecules are lost from the crystals. Also, it is unlikely that oxygen vacancies persist in the crystal after reduction, or that they order onto {10*m*} planes. These steps should therefore be considered only in the light of providing a means of quantitatively analysing the formation energies of various {10*m*} *CS* planes.

Evaluation of Energy Terms

G_I

The terms in G_I represent the interaction terms between the *CS* plane and its surroundings, and for isolated *CS* planes these reduce to $(U_s)_I$, $(U_e)_I$, and entropy terms. Values of $(U_s)_I$ and $(U_e)_I$ have been calculated previously (*6*, *8*) and we will not repeat the details of these calculations here, but simply report the results obtained, together with some of the limitations of the calculations.

$(U_s)_I$

In order to evaluate $(U_s)_I$, one should ideally calculate the strains of all ions in the crystal, but this is clearly impractical. Thus, in this calculation, we consider only those ions which lie between the *CS* plane and a position which is separated from the center line of the *CS* plane by a distance of 21.5*a*. It also follows that the strain of each ion should ideally be the summation of the strains due to all of the units of edge-shared octahedra in the *CS* plane. This calculation is also impractical, so we have chosen to sum only the strains due to 17 × 41 units in the case of a {104} *CS* plane, 15 × 41 units in the case of a {105} *CS* plane, 13 × 41 units in the case of a {106} *CS* plane, and 11 × 41 units in the case of a {107} *CS* plane. For {102} and {103} *CS* planes, we have calculated values of $(U_s)_I$ previously (*8*). To obtain a value of $(U_s)_I$, for {001} *CS* planes we have chosen a slightly different procedure than that described in (*8*) and replaced the {001} geometry by a {10*m*} *CS* plane of indices {10,81}. The calculation then uses an area of *CS* plane given by 1 × 41 units, which has an area virtually identical to that used in all of the other calculations. The value of $(U_s)_I$ obtained in this way differs very slightly, but not significantly, from that reported earlier (*8*). In all these calculations the units which give the largest strain, as expected, lie in the center of these blocks and in the present calculations it was found that the ratio of the strain due to a unit in the boundary to the strain due to a unit in the center was less than 0.01.

In order to evaluate $(U_s)_I$ we chose to calculate the elastic strain energy E_s in rows of octahedra parallel to the center line of each *CS* plane type and then to sum all the resultant values (see, e.g., (*6*)). In the case of a {10*m*} *CS* plane, there are $(m + 1)$ octahedra parallel to each unit which have their centers at a distance of $(2N + \frac{1}{2})a$ from the center line in each unit, where N is a positive integer. The average value of the strain energies of the $(m + 1)$ octahedra, $E_s(N)$, is related to $(U_s)_I$ by the following equation.

$$(U_s)_I = \frac{2 \times 2^{1/2}(m+1)}{a^2[(m-1)^2 + (m+1)^2]^{1/2}} \sum_{N=1}^{\infty}{}' E_s(N). \tag{3}$$

In Fig. 2. we have shown the relation between $\sum E_s(N)$ and N of each *CS* plane. In this figure, the vertical axis indicates $\sum E_s(N)/C$, where $C = (\lambda + 2\mu)(f/8\pi\mu)^2/(4\pi r_0^3/3)$ and the horizontal axis shows N. In plotting the curves in Fig. 2 we made the same assumption as our previous report, i.e.,

$$f_{102} \simeq f_{103} \simeq f_{104} \simeq f_{105} \simeq f_{107} \simeq f_{001} = f. \tag{4}$$

By extrapolating $E_s(N)$ to high N values in Fig. 2. the values of $(U_s)_I$ are found to be

$$102,\ (U_s)_I \simeq 0.2180\ C/a^2,$$

$$103,\ (U_s)_I \simeq 0.2490\ C/a^2,$$

$$104,\ (U_s)_I \simeq 0.2560\ C/a^2,$$

$$105,\ (U_s)_I \simeq 0.2360\ C/a^2,$$

$$106,\ (U_s)_I \simeq 0.2170\ C/a^2,$$

$$107,\ (U_s)_I \simeq 0.1990\ C/a^2,$$

$$001,\ (U_s)_I \simeq 0.0970\ C/a^2.$$

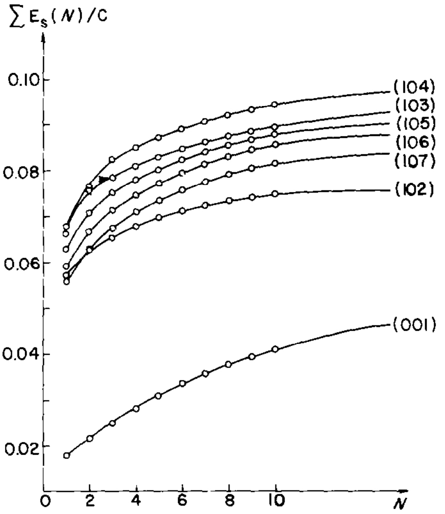

FIG. 2. The elastic strain energy for single *CS* planes in an ReO_3 matrix, $\sum E_s(N)/C$, as a function of N, the distance from the *CS* plane. The curves have been extrapolated to high N values.

Using the value $C/a^2 = 80$ eV nm^{-2} derived by Iguchi (*7*) we can convert these into absolute values. These values are listed in Table I and are also plotted in Fig. 3 as a function of m in $\{10m\}$.

TABLE I

SOME INTERNAL ENERGY COMPONENTS OF G_I AND G_d

CS plane indices	$(U_s)_I{}^a$ eV nm^{-2}	$(U_e)_I{}^a$ eV nm^{-2}	$U_d{}^a$ eV nm^{-2}
{102}	17.44	$-8.6 \times 10^{-3} \times (2 + \delta_{102})/2$	9.29
{103}	19.92	$-6.8 \times 10^{-3} \times (4 + \delta_{103})/3$	13.1
{104}	20.48	$-5.7 \times 10^{-3} \times (6 + \delta_{104})/4$	15.1
{105}	18.88	$-5.1 \times 10^{-3} \times (8 + \delta_{105})/5$	16.3
{106}	17.36	$-4.6 \times 10^{-3} \times (10 + \delta_{106})/6$	17.1
{107}	15.92	$-4.3 \times 10^{-3} \times (12 + \delta_{107})/7$	17.6
{001}	7.76	$-2.3 \times 10^{-3} \times (2 + \delta_{102})$	20.8

[a] 1 eV = 1.602×10^{-19} J.

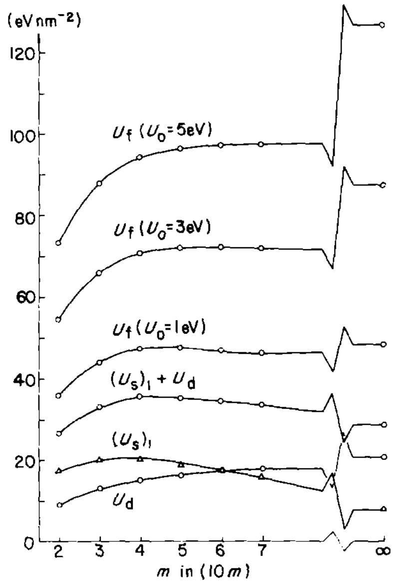

FIG. 3. The formation energy, U_f, elastic strain energy, $(U_s)_I$, and dissociation energy, U_d, for $\{10m\}$ *CS* planes in the ReO_3 structure as a function of m. See text for details.

$(U_e)_I$

We have evaluated this term in the formation energy by assuming that each block of m edge-shared octahedra comprising a unit of a $\{10m\}$ *CS* plane has a charge of $\{2(m-1) + \delta_{10m}\}e$. This charge is assumed to be distributed within each *CS* plane unit in a way similar to that in (*8*). As experimental values of δ, the amount the charge in the *CS* plane units differs from that expected on a purely ionic model is totally unknown, it has been left in the results as a multiplying factor. The results obtained in this way are listed in Table I. It can be seen from these values that even if the charges within the *CS* plane are quite different from those expected on an ionic model, the overall values of $(U_e)_I$ are much smaller than $(U_s)_I$ and can be ignored in the analysis.

G_d

The major internal energy terms in G_d are U_{self} and U_d. The energy U_d required to remove oxygen from WO_3 was estimated earlier from thermodynamic data to be about

4×10^{-19} J (2.5 eV) per oxygen atom. No experimental data is available for comparison as reduction of WO_3 does not seem to produce oxygen vacancies in the crystals. However Kofstad (*9*) has interpreted electrical conductivity data (*10*) to estimate the enthalpy of formation of oxygen vacancies in WO_3 to be about 3.0 eV. This value is similar to the value obtained from thermodynamic data, and for the estimates used in this paper a value of 3.0 eV will be used.

The value of U_d per unit area of a $\{10m\}$ *CS* plane can now be readily determined as $(m - 1)$ oxygen vacancies are needed to form a block of m edge-shared octahedra, with area $[\frac{1}{2}(m-1)^2 + \frac{1}{2}(m+1)^2]^{1/2}\, a^2$. U_d is therefore given by

$$(U_d)_{10m} = 3\{2^{1/2}(m-1)/[(m-1)^2 + (m+1)^2]^{1/2}a^2\}, \quad (5)$$

where a is the length of a diagonal of a WO_6 octahedron. The values so obtained are listed in Table II and are also shown in Fig. 3. It is clear that if the value of the energy needed to create the hypothetical vacancy array is significantly different from that used, the values quoted will also change, but the ratios of these values will always remain constant.

The final energy term to be evaluated is U_{self}. A number of factors are involved in U_{self} but none of them can be quantified with confidence. For our present purposes, we have considered that U_{self} will be made up of the two principle components, a potential energy term due to the interaction of the ions in the *CS* plane $(U_{self})_p$ and one due to the strain energy associated with the edge-shared octahedra in the *CS* plane $(U_{self})_s$. Thus U_{self} will have the form

$$U_{self} = (U_{self})_p + (U_{self})_s. \quad (6)$$

In a $\{10m\}$ *CS* plane the cations in the metal atom plane are brought closer together than in WO_3 itself. If we assume an ionic model for the *CS* plane structure it is a fairly simple matter to estimate the change in potential energy due to ionic interactions by using the approximations of Pauling (*11*) or Torrens (*12*) for the interionic potential between the ions involved.

In general, for a $\{10m\}$ *CS* plane there are $2m - 1$ cation–cation interactions to consider. The increase in potential energy per unit area of *CS* plane $(U_{self})_p$ then becomes

$$(U_{self})_{p\,10m} = 2^{1/2}(2m-1)(\phi_c + \phi_a)/[(m-1)^2 + (m+1)^2]^{1/2}a^2, \quad (7)$$

where ϕ_c and ϕ_a are the potential energies of the cations and anions respectively and a is the diagonal length of a WO_6 octahedron. In terms of an ionic model, the charges on the cations are at least double that on the anions so that we can make the further approximation that

$$[(U_{self})_p]_{10m} \approx 2^{1/2}(2m-1)\phi_c/[(m-1)^2 + (m+1)^2]^{1/2}a^2. \quad (8)$$

We take the energy due to the internal strain per unit area of a $\{10m\}$ *CS* plane to have a similar form to Eq. (7) for the following reasons. The WO_6 octahedra which form the *CS* plane are joined to each other by edge sharing and there are $(2m - 1)$ edges connecting these octahedra per unit of the $\{10m\}$ *CS* plane. In addition, these octahedra in the *CS* plane link up with WO_6 octahedra in the

TABLE II

VALUES OF THE TOTAL FORMATION ENERGY, U_f, FOR ISOLATED *CS* PLANES

	U_f (eV nm^{-2})		
CS plane	$U_0 = 1.0$ eV	$U_0 = 3.0$ eV	$U_0 = 5.0$ eV
{102}	36.02	54.60	73.19
{103}	43.97	65.87	87.77
{104}	47.34	70.85	94.37
{105}	47.40	71.85	96.30
{106}	46.98	72.03	97.08
{107}	46.25	71.72	97.18
{001}	48.15	87.32	126.50

matrix at corners and there are $6m$ corners connecting the octahedra in the *CS* plane with the octahedra in the matrix per unit of the $\{10m\}$ *CS* plane. If the strain energy due to an edge-sharing pair is denoted as U_{ed} and the strain energy due to a corner-sharing pair is denoted as U_{co}, the energy due to the internal strain per unit of the $\{10m\}$ *CS* plane is given by $(2m-1)\,U_{ed} + 6mU_{co}$. As the relaxation of the ions inside the *CS* plane will be obstructed by edge sharing, one can expect internal strain to be present and that $U_{ed} \gg U_{co}$. Thus, the energy due to the internal strain per unit area of a $\{10m\}$ *CS* plane can be expressed approximately by Eq. (9).

$$(U_{self})_{s\,10m} \approx (2m-1)\,U_{ed}/[\tfrac{1}{2}(m+1)^2 + \tfrac{1}{2}(m-1)^2]^{1/2}\,a^2. \tag{9}$$

From Eqs. (8) and (9), we can write Eq. (10),

$$(U_{self})_{10m} = (2m-1)\,U_0/[\tfrac{1}{2}(m+1)^2 + \tfrac{1}{2}(m-1)^2]^{1/2}\,a^2, \tag{10}$$

where $U_0 = \phi_c + U_{ed}$.

If ϕ_c is nearly independent of m in $\{10m\}$, $(U_{self})_{10m}$ increases smoothly as m increases and

$$(U_{self})_{102}/(U_{self})_{001} = 0.671. \tag{11}$$

Total Formation Energy, U_f

Experimental data indicate that $\{102\}$ *CS* planes should have the smallest formation energy of a series of $\{10m\}$ *CS* planes in WO_3. We can express this consideration in terms of the equations above by writing

$$\left\{[(U_s)_1]_{102} + (U_d)_{102} + \frac{3U_0}{10^{1/2}a^2}\right\} < \left\{[(U_s)_1]_{001} + (U_d)_{001} + \frac{2}{a^2}U_0\right\}. \tag{12}$$

The data in Table I show that Eq. (12) always holds for any positive values of U_0.

At present it appears difficult to obtain a realistic value of U_0 either theoretically or experimentally, but we can obtain an estimate of ϕ_c for the W–O binary system by using the interionic potential between ions given by Eq. (13), derived from Pauling (*11*) and Torrens (*12*).

$$\phi(r) = q_i q_j e^2/\varepsilon r + \alpha \exp(-\beta r), \tag{13}$$

where q_i and q_j denote the charge of ions i and j, r is the separation between them, and ε is the dielectric constant of the medium between the ions. To evaluate $\phi(r)$ approximately, we consider the *CS* plane to be neutral and also that every cation has an equivalent charge. We have used a value of $\varepsilon = 300$, as in our previous calculations (*8*). The separation between the cations, r is equal to $0.38/2^{1/2}$ nm in the idealized structure. To complete the data, we have taken the constant terms α and β for W as being equal to those calculated by Torrens (*12*). The results of the calculation yield

$$(\phi_c)_{102} = 4.98 \text{ eV}.$$
$$(\phi_c)_{001} = 4.89 \text{ eV}. \tag{14}$$

As we cannot be certain that the constants α and β can be applied to W ions in an ionic crystal of WO_3 there will be some uncertainty in the overall magnitude of these values. Nevertheless, they serve to suggest that Eq. (12) has a high possibility of holding.

The total formation energy U_f has been tabulated in Table II taking values of U_0 to be 1.0, 3.0, and 5.0 eV and these values are shown diagrammatically in Fig. 3, plotted as a function of m in $\{10m\}$. As can be seen from this figure, the formation energy increases from $m = 2$ to a maximum at a value which depends upon U_0. Further increase leads to a smooth decrease in the formation energy and then to a further increase.

Discussion

Our results suggest that there are a number of factors controlling the formation energy of *CS* planes in a WO_3-like matrix and that a simple discussion in terms of the energy required to remove oxygen from the crystal, U_d, as was originally suggested (*5*) is not sufficient to explain the stability of {102} *CS* planes over the other {10*m*} types. Nevertheless, this term is very important. It is of the same order of magnitude as the term $(U_s)_1$ and it compensates for the trend in $(U_s)_1$ values sufficiently to make {102} *CS* planes those with the lowest formation energy, even if the U_0 term is zero. One must, though, treat these magnitudes with some caution. One of the difficulties in comparing the values of $(U_s)_1$ and U_d is the number of uncertainties involved in the evaluation of the energies in absolute terms. Clearly if the values of U_d are doubled or $(U_s)_1$ are halved, then this would make a big difference to the relative stabilities of the {001} and {102} *CS* planes. Under these circumstances the value chosen for U_0 would be more significant.

One feature of the calculations is that if U_0 is fairly small the balance between {102} *CS* formation and {001} *CS* formation seems fairly delicate. One would expect, therefore, that if a variety of ReO_3 type structures were considered, the only two *CS* plane types that would be likely to form initially would be either {102} or {001}. This is in good agreement with the experimental data. WO_3, either reduced or doped with lower valent cations, always seems to form {102} *CS* planes on initial reduction. The material NbO_2F, which possesses the ReO_3 structure, certainly favors reduction by way of {001} *CS* planes (*13*). Our results also suggest that if the formation energy of {001} *CS* planes is lower than that for {102} *CS* planes, it will be lower than for all {10*m*} *CS* planes. Therefore continued reduction should lead only to {001} based *CS* phases, and not to a change in *CS* plane orientation, as occurs in WO_3 itself. Such a prediction also accords well with the literature. In evaluating this result, though, one must bear in mind that Nb^{+5} ions would be expected to show a preference for continuous strings of edge-sharing octahedra. This preference seems to be revealed, for example in the $Nb_2O_5:WO_3$ *CS* phases (*14*), so that other factors such as cation–cation bonding may also be responsible for altering the balance.

In the reduction of WO_3, {102} *CS* planes are replaced by {103} *CS* planes as the oxygen to metal ratio falls. Although this situation is best treated in terms of arrays of *CS* planes, the fact that {103} *CS* planes form instead of {001} *CS* planes suggests that U_0 for the WO_3 matrix may lie in the region between 0.0 and 1.0 eV. Figure 3 shows that such a value could make the formation of {103} *CS* planes less favorable than {102} and more favorable than {001}. Other aspects of the formation and stability of arrays of *CS* planes will be found elsewhere (*15*).

In general it is true to say that only two types of isolated *CS* plane have been found in WO_3-like materials, {102} *CS* in the WO_3 based oxides and {001} in NbO_2F. If one considers, though, the formation of *CS* planes in a matrix already containing other *CS* planes, another factor becomes important. This is the interaction energy between the new *CS* plane and others which may be nearby. There are two ways in which this additional energy term can affect the formation of the new *CS* plane, it can either influence the position where it nucleates, or else it can modify its geometry. The first of these factors has been dealt with elsewhere (*6*) and it was shown that new *CS* planes are nucleated at a position of minimum elastic strain in the matrix. We will consider the second case here.

It was pointed out in a previous communication (*16*) that if a *CS* plane forms in an array of *CS* planes, its direction will vary with the spacing of the neighboring *CS* planes. For instance, if the array is of {103} *CS* planes, a new *CS* plane growing between a pair of neighboring *CS* planes will have indices of {102} if the *CS* planes in the array are widely spaced but will have indices of {103}, and will be parallel to the array, if they are closely spaced. At intermediate spacings the new *CS* plane tends to wander, and is made up

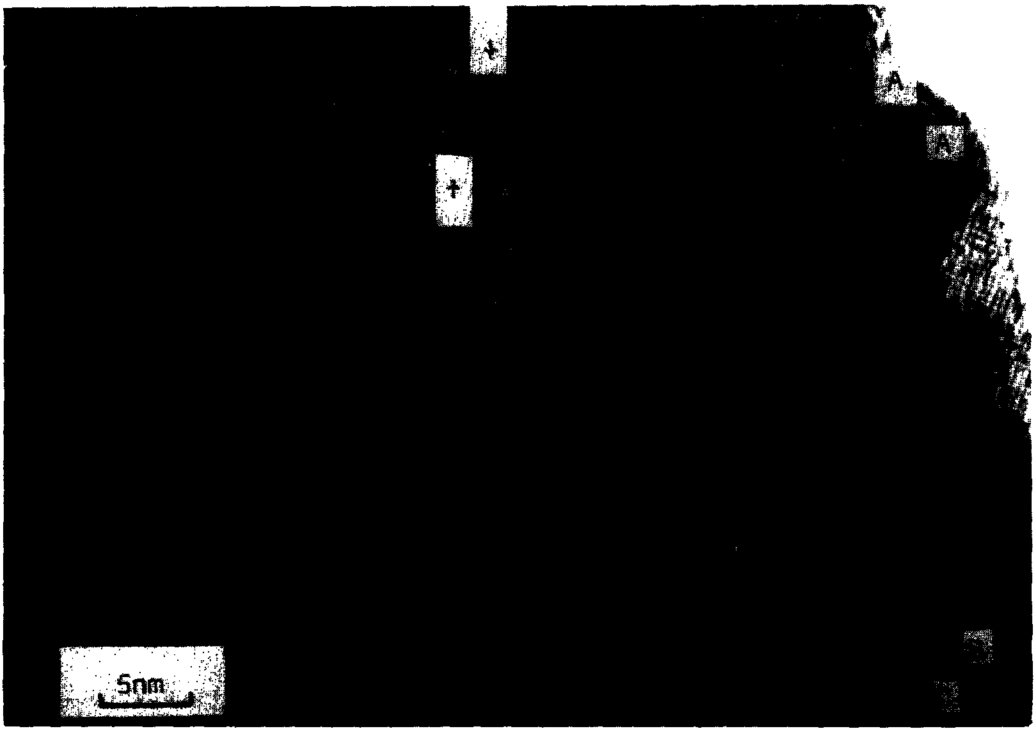

FIG. 4. {103} *CS* planes in a reduced WO_3 crystal. The *CS* planes marked A have nucleated and grown between relatively widely spaced existing *CS* planes during observation. It is seen that the central part of the new *CS* planes, arrowed, where nucleation started, lies on {102}, while further growth has caused the *CS* plane to swing into a {103} orientation. The freshly nucleated *CS* plane B was formed between neighbors with a smaller separation than A, and so has formed upon {103} initially. The *CS* plane C, which has also grown into the crystal, wanders in position slightly and contains both {102} and {103} units.

of {102} and {103} components. Figure 4 shows the nucleation of new *CS* planes in an array of {103} *CS* planes to illustrate this point.

In terms of our analysis, the formation energy U_f now contains an additional expression due to *CS* plane interactions, and which forms part of the overall G_1 term. If we treat the *CS* planes as being neutral, then it would appear reasonable to suppose that the most important factor here will be the elastic strain energy of the matrix between the new *CS* plane and its neighbors, generally represented by the symbol $(U_s)_2$, analogous to the $(U_s)_1$ term described earlier in this paper. The magnitude of the $(U_s)_2$ terms for various *CS* plane types and *CS* plane spacings have been given elsewhere (*15*). However, for the present purposes it is sufficient to note that $(U_s)_2$ is of the same order of magnitude as $(U_s)_1$ and that in the range of *CS* plane spacings of interest, for say, an oxide containing an array of {103} *CS* planes of composition about $W_{25}O_{73}$, $(U_s)_2$ for a {102} *CS* plane is about the same as $(U_s)_2$ for a {103} *CS* plane.

Thus, in simple terms, the addition of a $(U_s)_2$ term to U_f will not discriminate in favor of {103} *CS* planes over {102} *CS* planes. However, the experimental evidence suggests that the elastic strain energy, $(U_s)_2$ does control the position of the new *CS* plane. The difference between the two instances is that if a {102} *CS* plane starts to grow between neighboring {103} *CS* planes the growing *CS* plane continually approaches its neighbors, with a resulting rapid increase in the elastic strain energy density in the matrix. When a parallel {103} *CS* plane grows the strain energy is constant at all times. Thus, if the spacing between the *CS* planes is not too narrow, the new *CS* plane will tend to grow on {102}, but the strain energy at the tip will increase so rapidly that it will become higher than if the *CS* plane reverts to a {103} orientation, or else diverts to another {102} plane. This behavior is typical of the irregular *CS* planes which wander from side to side. If the *CS* plane spacing is narrower then it is possible that any deviation from a {103} orientation creates too great a strain field, and so the new *CS* plane grows in an effectively straight line. This behavior is illustrated in Fig. 4. Thus there are circumstances when the formation energy of a *CS* plane can be altered locally due to a high strain energy density, although if these local constraints were removed the favored *CS* plane type would once again predominate.

In conclusion we can say that our calculations suggest that a number of factors are important in controlling which of the various {10*m*} *CS* plane types form on reduction of a WO_3-like matrix, but in general they suggest that the only two types likely to be encountered are {102} or {001} *CS*. We are planning further experiments to attempt to check some of these factors. In addition, a following communication describes the effect that the formation energy has upon the expected microstructures to be found in crystals containing ordered arrays of *CS* planes.

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