Strain Energy due to {001} Crystallographic Shear Planes in Materials Possessing the ReO₃ Structure

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The elastic strain energy in a structure of the ReO₃ type containing ordered arrays of {001} CS planes has been calculated. The values obtained are for the elastic strain energy of the matrix between CS planes and also the relaxation energy of the ions in the CS planes themselves. Interactions from all the CS planes in the crystal are summed and not just those from nearest neighbors. The extent to which the CS planes can be considered to transmit the forces which strain the crystal is considered by including a variable parameter, α, in the calculations, which is related to the type of chemical bonding present in the CS planes. The results are compared with experimental observations in the WO_3–Nb_2O_5 and NbO_2F systems. It is concluded that the value of α is high for WO_3 doped with Nb_2O_5 and low for NbO_2F in accord with the expectations of chemical bonding. The results also support the view that elastic strain energy is important in influencing the microstructures observed in crystals containing CS planes.

Introduction

In recent years a substantial amount of experimental evidence has been presented concerning the crystal chemistry of the crystallographic shear (CS) structures which are formed when WO_3 crystals are reduced or doped with certain other metals (see, for example, the review articles by Anderson (*1*); Tilley (*2, 3*); Anderson and Tilley (*4*); and Iguchi and Tilley (*5*)). It is only recently, however, that these experimental results have been examined more quantitatively from the point of view of theoretical solid state chemistry and physics.

In such an analysis, there are a number of factors to consider. As CS planes are extended lattice defects it is likely that elastic strain energy is important, and indeed, such a suggestion was made some time ago by

Anderson (*6*). In addition to this factor we must also consider the real valence states of the ions within the CS planes. If the CS planes are not electrically neutral overall, a repulsive Coulomb energy will exist between CS planes while even if they are neutral there will still be an electrostatic interaction between the ions in the CS plane and those in the surrounding matrix (*7*). In addition, the observed fact that CS planes seem only to form in oxides which have high dielectric constants makes it possible that polarization effects play an important role as well (*8*).

Theoretical attempts to treat electronic interactions and polarization effects are at present underway, but are hampered in part by lack of precise experimental data concerning the valence states of ions in crystals containing CS planes. Thus the quantitative analysis of the behavior of CS

structures has been dominated by attempts to calculate elastic strain energy terms. Fortunately these have been shown to predict microstructures in fairly good agreement with experimental results (see, e.g., (5)) and indicate that Anderson's original suggestion to this effect was reasonable.

There are, at present, two approaches to the calculation of elastic strain in the literature. The first is that used by Stoneham and Durham (9), who evaluated the relaxation energy of ions in {001} CS planes formed in an ReO₃ type of crystal structure. In this model, forces were postulated to occur within each CS plane and the interaction between these forces lead to the relaxation. According to this model the crystal matrix between CS planes only transmitted these forces and at no time was it considered to undergo elastic strain. In the second approach, that of Iguchi and Tilley (5), forces were also assumed to occur within the CS planes principally as a result of cation–cation interactions. These forces were considered to strain the crystal matrix surrounding the CS planes, which was considered to be an isotropic continuum. When treating arrays of CS planes, only the elastic strain in the matrix between two CS planes was considered and cumulative effects due to other CS planes was totally neglected. They did not calculate the relaxation energy of the ions within the CS planes due to the forces postulated to occur in the neighboring CS planes.

These two approaches are to a large extent complementary. The first point which is apparent is that the true elastic strain energy of a crystal containing CS planes should be a summation of both the relaxation energy of ions within the CS planes and the elastic strain energy of the crystal matrix lying between the CS planes, and therefore we should evaluate both terms. Second, Stoneham and Durham treated the region within the CS plane as a continuous medium, as well as the matrix between CS planes and, there-

fore, they assumed that the CS plane could transmit forces perfectly without any damping. If we define α as the permeability of the forces in one CS plane, in their model $\alpha = 1$. On the other hand, Iguchi and Tilley assumed that $\alpha = 0$, as their model for a CS plane involves discrete ions. It is certainly possible that α lies between these values, and it may therefore be possible to obtain information on the nature of CS planes by treating α as a parameter in the theoretical calculations and comparing the results with experimental data.

The present paper describes the results of such calculations. In order to present the findings concisely we have chosen in this instance to consider only the simplest geometrical situation, that is, the case of {001} CS planes in an ReO₃ (DO₉) type of crystal structure. Energy terms due to a pair of {001} CS planes and an infinite array of {001} CS planes have been evaluated. These values are presented here and discussed in the light of the available experimental data. A following communication will use the results given here in evaluating the elastic strain energy and relaxation energy for other CS plane geometries in reduced WO₃.

Theory

The ReO₃ structure consists of an infinite array of corner-sharing metal–oxygen octahedra as shown in Fig. 1a. It is cubic, with a lattice parameter, a, equal to an octahedron diagonal. Although ReO₃ has not been observed to support reduction by way of CS, the isostructural NbO₂F does, and reduction of this compound leads to CS plane formation on {001} (10). The idealized structure of an {001} CS plane is shown in Fig. 1b. In NbO₂F, these CS planes are usually present in fairly low densities, but phases geometrically derived from NbO₂F by ordered CS, such as Nb₂O₇F, are also known and it is possible that under carefully controlled experimental conditions a wide
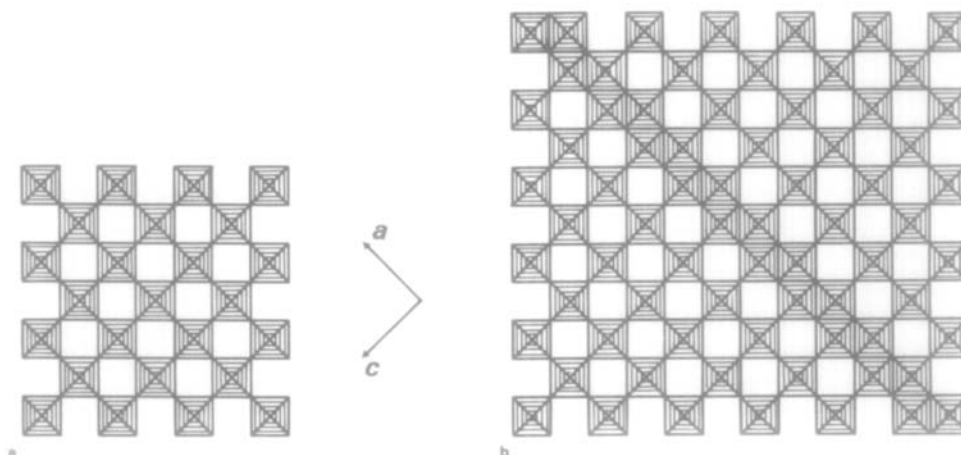
FIG. 1. Idealized representations of: (a) the cubic ReO_3 structure type; and (b) an $\{001\}$ CS plane in a matrix of the ReO_3 type. The shaded squares represent metal–anion octahedra which are joined by corner sharing to form a three-dimensional array. The axes marked are those of the cubic unit cell of ReO_3.

range of $\{001\}$ CS phases might form in the Nb–O–F ternary system although previous experiments to this end have proved unsuccessful (11).

Also related to the ReO_3 structure is WO_3. In this material the cations are off-centre and the structure somewhat distorted so as to reduce the symmetry to monoclinic, but topologically it remains identical to ReO_3. Reduction of WO_3 leads to an extensive series of CS phases (see, eg., (1–4)) but in this case the CS planes usually lie on $\{102\}$ or $\{103\}$ planes, referred to the idealized cubic unit cell. In the Nb–W–O and Ti–W–O ternary systems, however, ordered arrays of $\{001\}$ CS planes are observed (12, 20).

A crystal containing an ordered array of $\{001\}$ CS planes is a member of a homologous series of oxides of formula M_nO_{3n-1}. The value of n in this formula is simply the number of metal–oxygen octahedra separating each CS plane. In the absence of any distortion of the crystal, the spacing of the CS planes d_n is therefore related to n by the equation

$$d_n = (n - \tfrac{1}{2})a, \qquad (1)$$

where a is the length of the octahedron diagonal.

Figure 1b shows that within $\{001\}$ CS planes the cations and also the anions above and below them are much closer together than they normally are in the matrix. We assume that this close approach gives rise to repulsive forces, of which those between the cations are expected to be strongest. These forces, f, shown in Fig. 2, are the ones we assume to be responsible for the strain described in the Introduction. The first of these is due to the interaction of the forces in one CS plane with the forces in all the other CS planes. This effect is a work term
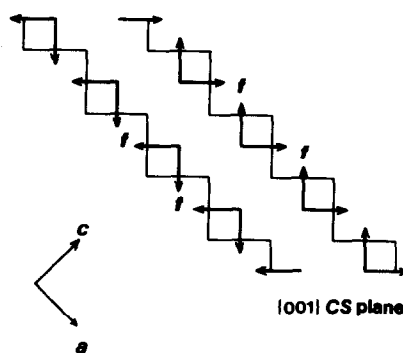

FIG. 2. Schematic representation of the forces in an $\{001\}$ CS plane which are supposed to give rise to elastic strain in the crystal.

expressed as the scalar product of the force acting on a cation in a *CS* plane with the displacement of this ion due to all other forces. If the cation displaces along the direction of the defect force acting on it, as would be expected, this will tend to counteract the increase in the elastic strain energy. For this reason we term this interaction a relaxation energy, U_R. The second energy term is simply the elastic strain in the matrix surrounding a *CS* plane due to the forces within the *CS* plane. This term we express as U_S. The total interaction energy, U, is therefore given by

$$U = U_S - U_R. \qquad (2)$$

To calculate these terms we take an idealized array of {001} *CS* planes as depicted in Fig. 3. The relaxation energy U_R of the forces in a unit area of *CS* plane *1* with all of the forces in all of the other *CS* planes is evaluated and then the strain energy, U_S, in the matrix between *CS* planes *1* and *1'* due to all the forces in the array is evaluated. These two terms are summed and then reduced to a value per unit volume of crystal.

In calculating these terms we have employed a permeability factor, α, as described above, to characterize the *CS* planes' ability to transmit the forces.

The energy, U_R, per unit area of the *CS* planes can be obtained as follows:

$$U_R = \sum_i (f_1)_i \boldsymbol{u}_i$$

$$= \sum_i (f_1)_i \left[\sum_{n=2} \alpha^{n-2} \left\{ \sum_j \boldsymbol{G}(f_n)_j \right\} \right.$$

$$\left. + \sum_{n'=1'} \alpha^{n'-1} \left\{ \sum_j \boldsymbol{G}(f_{n'})_j \right\} \right], \qquad (3)$$

where $(f_1)_i$ represents the *i*th force in a unit area of *CS* plane *1* and $\boldsymbol{u}_i$ is the displacement of the ion on which $(f_1)_i$ does work due to all the forces in all the *CS* planes except *CS* plane *1*. The notation $\sum_i$ indicates the summation of the interaction energy of all ions in a unit area of *CS* plane *1*. The *j*th forces in the *n*th *CS* plane or in the *n'*th *CS* plane are represented by $(f_n)_j$ or $(f_{n'})_j$, where *n* indicates the *CS* plane to the right of *CS* plane *1* and *n'* the one to the left, as shown in Fig. 3, and $\sum_j$ indicates the summation of
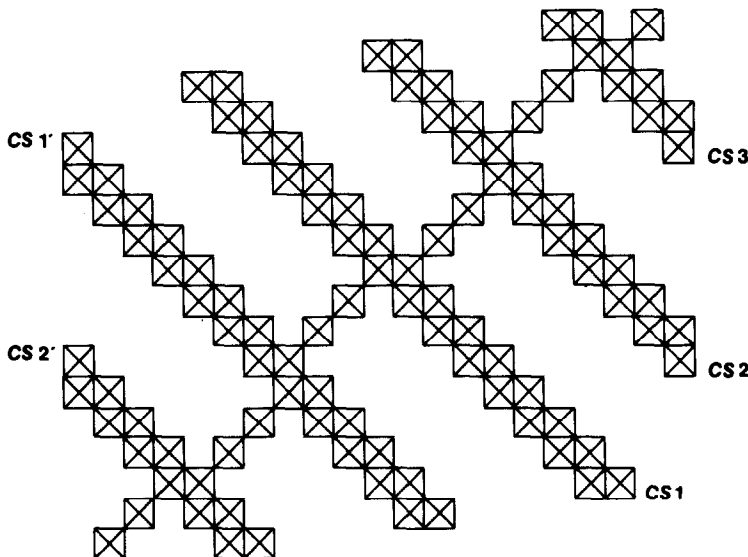

FIG. 3. An array of {001} CS planes in an ReO$_3$ type of crystal, showing the labeling of *CS* planes used in the text.

each component of the displacement of the ith ion in *CS* plane *1* due to the forces in the nth or n'th *CS* plane. In addition, $\sum_{n=2}$ means the summation of the displacement of the ith ion caused by all the *CS* planes to the right of *CS* plane *1* and $\sum_{n'=1}$ a similar summation due to all the *CS* planes to the left. In Eq. (3), G is the elastic Green's function and its ijth component has the form *(13)*

$$G_{ij} = (1/8\pi\mu)$$

$$\times \left\{ \delta_{ij}\nabla^2 r - \left(\frac{\lambda+\mu}{\lambda+2\mu}\right)\left(\frac{\partial^2 r}{\partial X_i \partial X_j}\right)\right\},$$

(4)

where r is the vector from the ion on which $(f_1)_i$ acts to the position of $(f_n)_j$ or $(f_{n'})_j$ and λ and μ represent the Lamé constant and the shear modulus, respectively.

The strain energy, U_S, in the matrix between *CS* planes *1* and *1'* can be obtained as follows. The displacement of an ion in the matrix is evaluated by

$$u = \sum_{n=1} \alpha^{n-1}\left\{ \sum_j G(f_n)_i\right\}$$

$$+ \sum_{n'=1'} \alpha^{n'-1}\left\{ \sum_j G(f_{n'})_i\right\},$$

(5)

where every notation has a similar meaning to Eq. (4) except $\sum_{n=1}$ which indicates the summation of the displacement of an ion due to all the *CS* planes on the right-hand side of *CS* plane *1* which is included in this summation. We then have obtained each component of the strain of the ion in the matrix from the relation

$$e_{hk} = \frac{1}{2}\left(\frac{\partial u_h}{\partial x_k} + \frac{\partial u_k}{\partial x_h}\right),$$

(6)

where e_{hk} is the hkth component of the strain e and u_h is the hth component of the displacement u.

When a unit-volume element deforms reversibly by the strain increment de_{ij}, the strain energy density function is obtained by

the integration of the work that the stress does on the element and, for a cubic crystal, the strain energy density is given as follows *(14)*:

$$w = \int \sigma_{ij}\, de_{ij}$$

$$= \frac{1}{2}(\lambda + 2\mu)\left\{ \sum_{i=1}^{3} e_{ii}\right\}^2$$

$$+ \mu \sum_{i,j=1}^{3} (e_{ij}^2 - e_{ii}e_{jj}), \quad (i \neq j).$$

(7)

Therefore, the strain energy in the matrix per unit area of the *CS* plane, U_S, is given by

$$U_S = \sum_i \frac{4\pi}{3}(r_I)^3 w_I,$$

(8)

where w_I is the strain energy density of the Ith ion in the matrix and r_I is its ionic radius and $\sum_I$ indicates the summation of the strain energy of all the ions in the matrix between *CS* planes *1* and *1'*.

A crystal which has an infinite ordered array of {001} *CS* planes has an energy per unit volume due to the forces in the *CS* planes, U_V, given by

$$U_V = (U_S - U_R)/d_n$$

$$= \left\{ \sum_I \frac{4\pi}{3}(r_I)^3 w_I - \sum_i (f_1)_i u_i\right\}\bigg/ (n - \tfrac{1}{2})a.$$

(9)

Calculations and Results

In order to evaluate U_S and U_R we will use the elastic Green's function as shown in Eq. (4), which indicates that the calculation will be performed in real space rather than Fourier space. This method has been adopted for the following reason. As described in the preceding section, the relaxation energy term due to the interaction of forces in any *CS* plane with themselves (i.e., the forces in *CS* plane *1* in Fig. 3) and the elastic strain energy caused by the forces acting on ions within the *CS* planes themselves (the U_{self} term in *(5)*) will not be included in the initial

calculations. The reason for this is that it is important to reveal the extent to which we can treat the CS plane itself as a continuous medium in the same way as we hav. treated the matrix between CS planes. If the CS plane can be treated as a continuous medium, then the permeability of the forces within one CS plane will have a value of the permeability coefficient α equal to 1.0. In such a case the Fourier transform method used by Stoneham and Durham (9) and Shimizu and Iguchi (15) can be applied. However, this is by no means certain, and if we need to change the value of α from 1.0 it becomes difficult to apply Fourier transform methods.

In calculating Eqs. (3) and (8) or Eq. (9), we have employed the same values for the relevant physical constants as in previous reports (5, 9); viz.,

$C_{11} : C_{12} : C_{44} = 16 : 7 : 5$,
r_O (the ionic radius of O ions) = 0.140 nm,
r_W (the ionic radius of W ions) = 0.060 nm.

Calculation of U_R

Initially consider a pair of parallel {001} CS planes *1* and *2*. The interaction energy $(U_R)_2$ of the forces in a unit area of CS plane *1* with all the forces in CS plane *2* is given by

$$(U_R)_2 = \sum_i (f_1)_i \left\{ \sum_j G(f_2)_i \right\}, \qquad (10)$$

where $\sum_j G(f_2)_i$ indicates the summation of the displacement of the ith ion on which the force $(f_1)_i$ does work due to all the forces in CS plane *2* and $\sum_i$ has the same meaning as in Eq. (3). We need to obtain the relation between $(U_R)_2$ and the spacing of the CS plane pair. In Eq. (10), we should sum the displacement of the ith ion caused by all the forces in CS plane *2* theoretically, but this is clearly impractical. Thus we have summed the displacement of the ith ion caused by the forces in a block which has a length of 301 a in the [001] direction and a height of 201 a in the [100] direction. In order to investigate

how appropriate this block size is we calculated the absolute values of the interaction energy, $\sum_i (f_1)_i G(f_2)_j$, between the forces in a unit area of CS plane *1* and the jth force on a line in the [001] and [100] directions which pass through the center of the block when the spacing between the pair is 3.5 a. These results showed clearly that the absolute value of the ratio of the interaction energy due to a force in the boundary of the block to the maximum interaction energy on these lines is less than 1×10^{-4}, which indicates the approximation employed in the calculations to be reasonable.

Using these approximations we have calculated $(U_R)_2$ for a range of values from $n = 4$ to $n = 110$ and plotted the result in Fig. 4. In this figure n is the value of n in $M_n O_{3n-1}$ and given in Eq. (1) which would apply if an
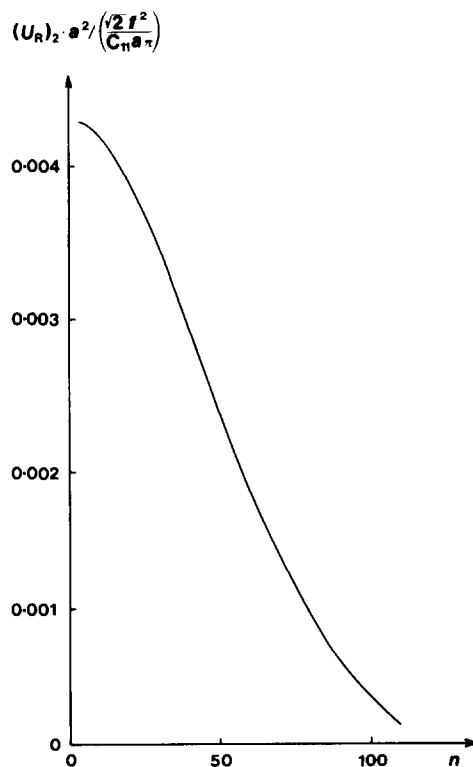

FIG. 4. The relationship between the relaxation energy of ions in a pair of CS planes, $(U_R)_2$, and the spacing between the CS planes, n.

infinite array of *Cs* planes were formed with the same spacing as the original pair. From the calculations it was found the $(U_R)_2 (110)/(U_R)_2 (4)$ is less than 0.1, where $(U_R)_2 (N)$ indicates the interaction energy when the *n* value is *N*. In order to calculate U_R for an array of *CS* planes it is necessary to calculate $(U_R)_2$ for the geometrical situation which represents the out of phase arrangement of *CS* plane *1* with respect to *CS* plane *3* (see Fig. 3). We will term this pair of *CS* planes incoherent, and we denote this energy term as $(U_R)_2'$. The variation of $(U_R)_2'$ with *n* closely parallels that of $(U_R)_2$ shown in Fig. 4. The relaxation energy per unit area per plane, U_R, for an infinite ordered array of {001} *CS* planes in a crystal whose composition is $M_n O_{3n-1}$ can then be represented by a summation of $(U_R)_2$ and $(U_R)_2'$ terms, that is,

$$U_R = 2\left\{ \sum_{i=1} \alpha^{2(i-1)}(U_R)_2(l_1) \right.$$

$$\left. + \sum_{i=1} \alpha^{2i-1}(U_R)_2'(l_2) \right\}, \quad (11)$$

where

$$l_1 = n + (2n-1)(i-1),$$

$$l_2 = (2n-1)i.$$

As shown in Fig. 4, $(U_R)_2 (N)$ *or* $(U_R)_2'(N)$ when $N > 110$ is negligibly small in comparison with $(U_R)_2 (4)$ *or* $(U_R)_2' (4)$ and we have neglected the contribution of $(U_R)_2 (N)$ or $(U_R)_2' (N)$ to U_R when $N > 110$. Thus we have considered the summation, $\sum_i$, for *i* lying in the range $i = 1$ to the maximum integer which satisfies $N_1 \leqslant 110$. Under these conditions, we obtain the result shown in Fig. 5.

Calculation of U_S

The method of calculating U_S has been described in detail in a previous paper (*5*). In this report, however, we have changed the method of calculation slightly, as follows. Here we have replaced the infinite chain of edge-shared pairs of MO_6 octahedra which make up the {001} *CS* plane by a *CS* plane

which effectively has indexes {10*m*}, where $m = 85$ and is made up of blocks of edge-shared octahedra 85 pairs long. Each one of these blocks is treated as one unit and we have summed the displacement of an ion in the matrix caused by all the units in an area of *CS* plane containing 41×1 units. In order to check whether this approximation is reasonable we have also performed some calculations using a *CS* plane in which $m = 87$ and an area containing 43×1 units in which each unit consists of 87 pairs of edge-sharing octahedra. Good agreement was found between the two resulting values, and the absolute value of the ratio of the difference between the strain of the metal ions which are nearest to the centre of these latter blocks to the strain of the metal ions which are nearest to the centers of the blocks containing 41 pairs of edge-shared octahedra is less than 1×10^{-3}.

In our earlier paper on this topic (*5*) we assumed that the strain energy of the matrix lying between a pair of *CS* planes, $(U_S)_2$, was not influenced by other *CS* planes in the crystal. The total elastic strain energy of the matrix of a crystal containing an array of *CS* planes was then simply approximated to the sum of all the individual $(U_S)_2$ values. In this paper we assume, as for U_R, that all the *CS* planes in the crystal influence the strain energy between any particular pair of *CS* planes. This means that the method of assessing the strain energy between a pair of *CS* planes must be somewhat different than previously. Again we make use of the "incoherent" *CS* plane geometry, as earlier.

Thus, to calculate the strain energy in the matrix per unit area of *CS* plane between the *CS* planes *1* and *1'* shown in Fig. 3 due to all the *CS* planes in the crystal we need to evaluate first the strain of the *I*th ion in the array of octahedra which extends to infinity from the center of each unit of 41 edge-shared pairs of octahedra. The *hk*th component of this strain is denoted as e_{hk}. It is then necessary to evaluate a similar term,
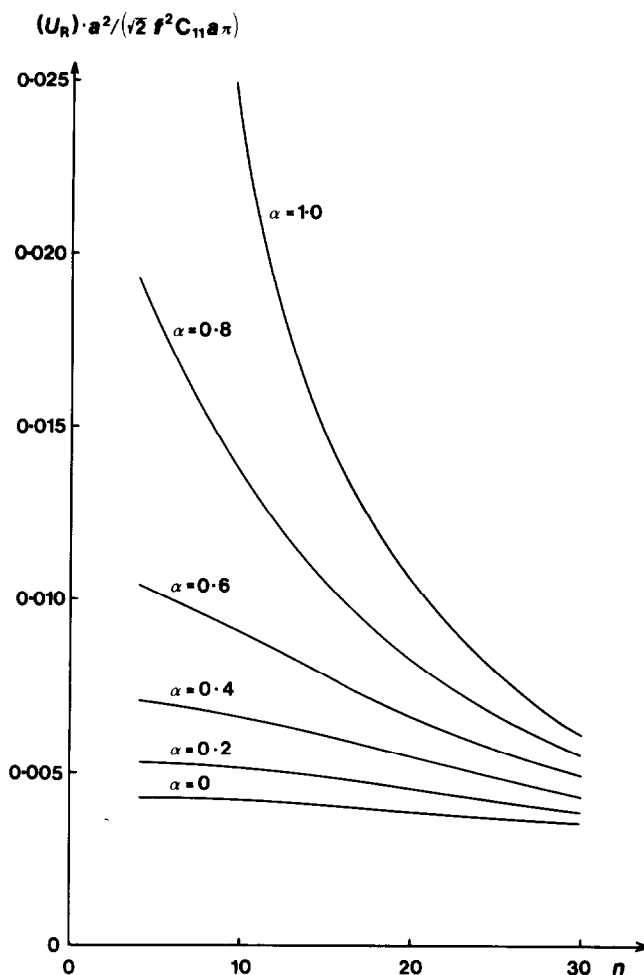
$(U_R) \cdot a^2 / (\sqrt{2}\ f^2 C_{11} a \pi)$

FIG. 5. The relationship between the relaxation energy of ions in a CS plane in an array of CS planes. U_R, as a function of the spacing between the CS planes, n, and the parameter α.

denoted e'_{hk}, for the equivalent incoherent array. We can now add these terms so as to reproduce the strain energy of the Ith ion in the matrix between CS planes 1 and $1'$ due to interactions from all CS planes in the crystal $[e_{hk}]$. The form this takes is given by

$$[e_{hk}] = \sum_j \{(\alpha^{2(j-1)}[e_{hk}(J_{2j-1})])$$
$$+ (\alpha^{2j-1}[e'_{hk}(J_{2j})])$$
$$+ (\alpha^{2(j-1)}[e_{hk}(J'_{2j-1})])$$
$$+ (\alpha^{2j-1}[e'_{hk}(J'_{2j})])\}, \qquad (12)$$

where $e_{hk}(J_{2j-1})$ indicates the hkth component of the strain of the Ith ion caused by the $(2j-1)$th CS plane in Fig. 3 and J_{2j-1} indicates the site number of the Ith ion which is counted from the $(2j-1)$th CS plane. In addition $[e_{hk}(J_{2j-1})]$ refers to the contribution from the coherent array of octahedra and $[e'_{hk}(J_{2j})]$ to the incoherent array to the right of CS plane 1, and $[e_{hk}(J'_{2j-1})]$ and $[e_{hk}(J'_{2j})]$ refer to the contribution from the coherent and incoherent array to the left of CS plane $1'$. The other notations in Eq. (12) have similar meanings.

Ideally we should calculate the strains in e_{hk} and e'_{hk} from the site nearest the *CS* plane unit to infinity. As this is impractical we have calculated the strains of the ions in sites from nearest the units out to a distance of $75a$ from the unit. The results of these calculations show that the ratio $e'_{hk}(75a)/e'_{hk}(1a)$ or $e_{hk}(75a)/e_{hk}(1a)$ is less than 0.03, where $e_{hk}(Na)$ indicates the hkth component of the strain of the Ith ion which is located at a distance of Na from the unit.

In a similar way, we should make the summation in Eq. (12) run from 1 to infinity. In this case we have summed the strain due to

those *CS* planes in a region $(2j-1)$ running from 1 to 75. The value of j which satisfies the relation $(2j-1)=75$ will, of course, vary as the n value describing the separation of the *CS* planes 1 and $1'$ varies.

The final value of U_S as a function of n is then obtained by substituting Eq. (12) into Eqs. (7) and (8). The results are shown in Fig. 6.

It is also of interest to compare the variation of the elastic strain energy between a pair of *CS* planes, $(U_S)_2$ with spacing. $(U_S)_2$ can be calculated in the following way. The displacement, u, of an ion in the matrix can

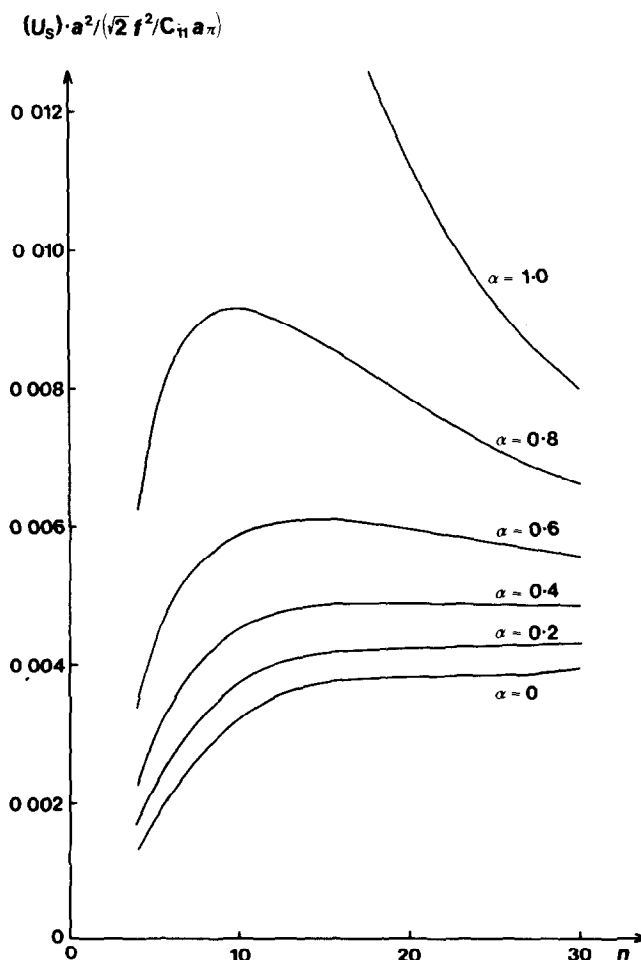$(U_S) \cdot a^2 / (\sqrt{2} \, f^2 / C_{11} \, a \, \pi)$

FIG. 6. The relationship between the elastic strain energy in the matrix between *CS* planes in an array as a function of the spacing between the *CS* planes, n, and the parameter α.

be represented by

$$u = \sum_{i=1}^{2} \sum_{j} G(f_i)_j, \qquad (13)$$

where $(f_i)_j$ denotes the jth force in the ith CS plane, $\sum_j$ indicates the summation of the displacement of the ion caused by all the forces in the ith CS plane, and $\sum_{i=1}^{2}$ indicates that we must sum the displacements due to both the first and second CS planes. We can obtain the strain energy by substituting Eq. (13) into Eqs. (6) and (9) and $(U_S)_2$ by using Eq. (10). In making the calculations we have employed the same conditions as those for the infinite ordered array. The results are shown in Fig. 8.

Total Energy of an Ordered Array, U_V

The energy per unit volume element due to an infinite ordered array of {001} CS planes, U_V, is given by Eq. (9). This has been plotted as a function of n in Fig. 7. In order to assess the real total strain energy we also need to include the strain energy within the CS planes themselves, termed U_{self} previously (5). This term is expected to be a constant which depends only upon the parameter α. At present it is possible to
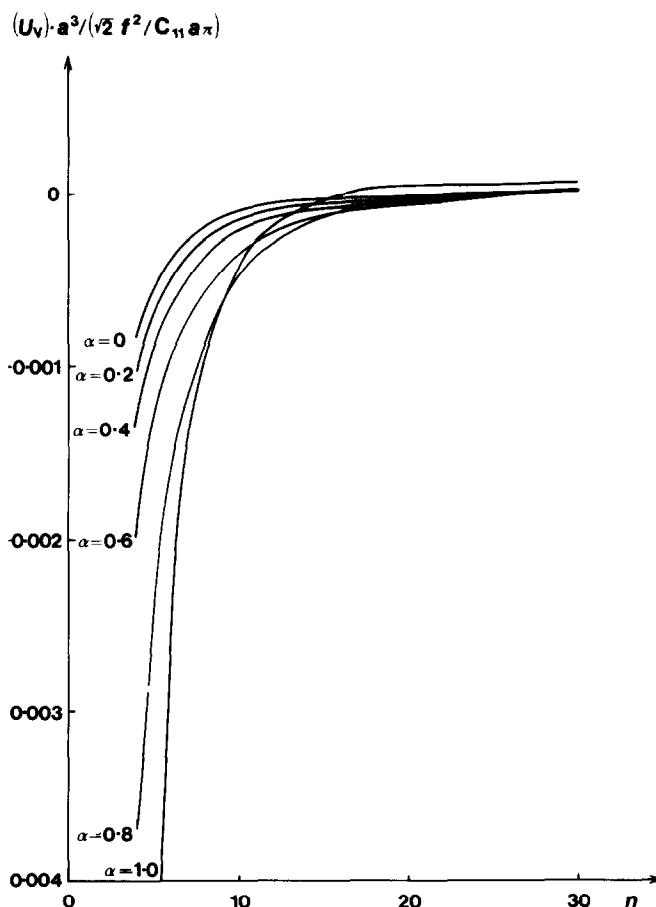

FIG. 7. The relationship between the total strain energy per unit volume, U_V, of an array of CS planes as a function of the spacing, n, between the CS planes and the parameter α.

evaluate U_{self} only for the case of $a = 1.00$. This procedure is outlined later.

Total Energy of a Pair of CS Planes, U_2

In our first report (5) we represented the increase in internal energy due to elastic strain arising from a pair of *CS* planes in a crystal as

$$U_2 = 2(U_S)_{self} + 2(U_S)_1 + (U_S)_2 \quad (14)$$

where $(U_S)_1$ represented the elastic strain energy in the matrix around an isolated *CS* plane, $(U_S)_2$ the elastic strain energy in the matrix between the pair of *CS* planes, and $(U_S)_{self}$ was the internal strain energy of the *CS* planes themselves.

We are now in a position to expand this equation somewhat, as Eq. (14) ignores the relaxation interaction $(U_R)_2$ between a pair of *CS* planes. Thus we can write

$$U_2 = 2(U_S)_{self} + (U_S)_2 + 2(U_S)_1 - 2(U_R)_2. \quad (15)$$

We have already calculated $(U_R)_2$ and $(U_S)_2$ earlier. We therefore need to estimate $(U_S)_1$. $(U_S)_{self}$ will be discussed later in this paper.

$(U_S)_1$ can be obtained by using Eq. (16), which is analogous to eq. (13) above.

$$u = \sum_j G(f_1)_j + \sum_j \alpha G(f_2)_j, \quad (16)$$

where the notation is the same as that used above. Substituting Eq. (16) into eqs. (6), (7), and (8) allows us to derive the strain energy in the matrix outside *CS* plane *1*, which is $(U_S)_1$. The strain energy in the matrix outside of *CS* plane *2* will be identical and also equal to $(U_S)_1$. In making the calculations we have only included the strain terms for the ions which are separated from the *CS* plane by a distance of not more than $76a$, as the strain energy of an ion located a distance of $75a$ from the *CS* plane is less than 2×10^{-3} of the strain energy of an ion nearest to the *CS* plane.

Thus we can evaluate most of the terms in Eq. (15). These are plotted in Fig. 8, which show $(U_R)_2$, $(U_S)_2$, and $(U_S)_1$, which have all been reduced to a value per unit area of *CS* plane, as a function of n. As the only term which contains α is $(U_S)_1$, Fig. 8 shows how $(U_S)_1$ varies with α. The total value of U_2 per unit area per plane excluding the U_{self} terms is shown in Fig. 9. Here the U_2 curve in the case of $\alpha = 1.00$ increases smoothly as n decreases below $n = 26$ and this curve has no maximum as the $\alpha = 0.80$ or 0.60 curves do. As described before, we should consider U_{self} in addition to U_2, but the shape of each curve in Fig. 9 would not change even if U_{self} were taken into account because U_{self} is a constant term which depends upon only the parameter α.

Discussion

The Relative Magnitude of U_R and U_S

In our previous communications concerning ReO$_3$-like lattices we have considered only the strain energy in the matrix between two *CS* planes. When arrays were considered, the total strain energy was simply assumed to be the sum of the strain energy between pairs of *CS* planes, with no consideration of interactions with *CS* planes other than these nearest neighbors. It is therefore of some interest to compare the present results with those given previously. In addition we have neglected the relaxation energy term in the past, and it is also useful to compare this energy term with the strain energy in the matrix to see whether one or other of these values dominates the energy totals.

A comparison of Figs. 5 and 6 is able to answer this latter point. It is seen that for higher n values the elastic strain in the matrix, U_S, is larger than the relaxation energy, U_R. At lower n values U_R is more dominant than U_S and there is a crossover somewhere between $n = 20$ and $n = 26$, the

$(U_B)_2$, $2(U_R)_2$, $2(U_S)_1$
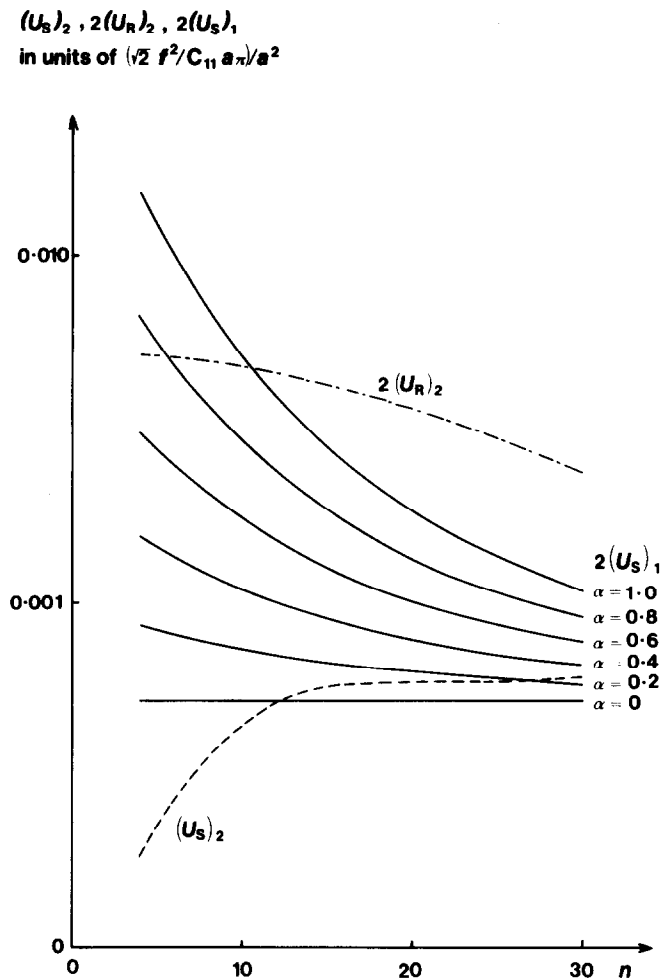in units of $(\sqrt{2}\ f^2/C_{11}\ a\pi)/a^2$

FIG. 8. The components of the elastic strain energy of a pair of CS planes as a function of the spacing between the CS planes, n, and the parameter α. See text for details.

precise point being dependent upon the value of the parameter α. This implies that both the elastic strain energy term and the relaxation term will have significance in controlling the microstructures of CS planes. A detailed consideration of this aspect of the energetics of CS plane formation for the important {102} and {103} derived series of CS phases found in the tungsten oxides is at present in progress.

In the case of $\alpha = 0.0$, the value of U_S is exactly the same as we obtained in the earlier calculations (16, 17). In the previous papers, however, the term U_S was expressed in units of C/a

$$C/a^2 = [(\lambda + 2\mu)(f/8\pi\mu)^2(4\pi r_0^3/3)]/a^2$$

which can be translated into the units of $(2^{1/2}f^2(C_{11}a\pi)/a^2$ employed in this report in the following way. As the unit of the length in the calculations of the strain energy, we have employed $a/2^{1/2}$, namely, the length of the edge of a MO_6 octahedron. In order to change the unit of the length from $a/2^{1/2}$ to nm, we have to change C/a^2 to $[C/(a2^{1/2})]/a^2$. Taking into account that $\lambda +$
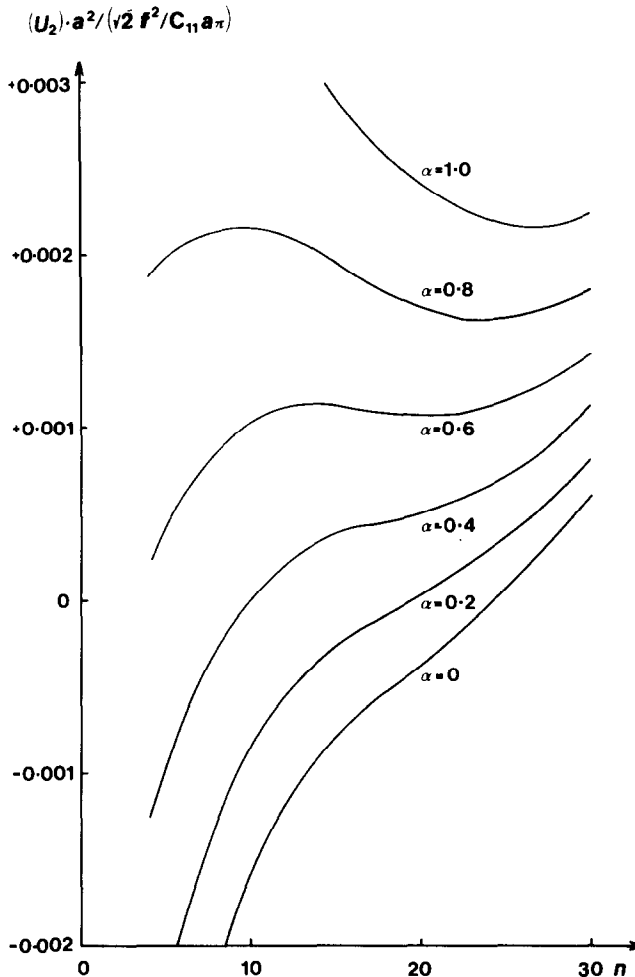
$(U_2) \cdot a^2 / (\sqrt{2} \, f^2 / C_{11} a \pi)$

FIG. 9. The relationship between the strain energy of a pair of *CS* planes, U_2, and the spacing between them, n, as a function of the parameter α.

$2\mu = C_{11}$, $\mu = C_{44} = (5C_{11}/16)$, and $r_O = 0.14$ nm, the following relation is obtained:

$$[C/(a/2^{1/2})^4]/a^2$$

$$= [(\lambda + 2\mu)(f/8\pi\mu)^2(4\pi/3)$$

$$\times (2^{1/2}r_O/a)^3]/(a/2^{1/2})/a^2$$

$$= 0.030174(2^{1/2}f^2/C_{11}a\pi)/a^2,$$

where we have taken that $a = 0.38$ nm. The unit $(2^{1/2}f^2/C_{11}a\pi)/a^2$ represents the energy per unit area. This shows that the principal strain energy in the matrix comes

from the nearest *CS* planes, that is, the pair that bound the particular region, and that other *CS* planes further away have a rather small contribution to make. The values reported previously can then be taken as very satisfactory approximations to those obtained by any more lengthy calculations of the type reported here.

The Value of α: Pairs of CS Planes

The results of the calculations for the interaction energy between a pair of *CS*

planes are shown in Figs. 8 and 9. The shape of the curves shown is markedly dependent upon the value of the parameter chosen and this in turn implies that a marked difference in microstructures will be found between materials in which a low value of α is applicable contrasted with those in which a high value pertains. Considering Fig. 9, one can see that, if α is small, namely, from $\alpha = 0.00$ to 0.40, the interaction energy between a pair of CS planes increases as the spacing between the CS planes increases. This is equivalent to the existence of an attractive force between the CS planes and suggests that any pair of CS planes would gain energy by approaching one another. On the other hand, for high values of the parameter α, the curves of interaction energy vs n are more complex. In the cases of $\alpha = 0.60$ and 0.80, each curve exhibits a peak and a valley. The curve for $\alpha = 1.00$ has a valley. This valley situated at approximately $n = 20$ in the case of $\alpha = 0.60$, $n = 24$ for $\alpha = 0.8$, and $n = 26$ for $\alpha = 1.0$ will represent a metastable separation of the CS planes. Ultimate stability in all of these cases, though, will tend to be at lowest CS plane separations.

Figures 8 and 9 only show the interaction between a pair of CS planes separated by up to $30a$. At greater separations we would expect that the interaction energy for all values of α would increase. This is because the decrease in $(U_S)_1$ becomes very small at such larger separations but $-2(U_R)_2$ continues to increase substantially, as shown in Fig. 5. In addition $(U_S)_2$ will tend to cause the total interaction energy to increase. We have calculated $(U_S)_2$ in the range $n = 3$ to 75 and found that the curve of $(U_S)_2$ vs n has a plateau in the range $n = 19$ to 28, increases smoothly from $n = 29$ to 63, and then decreases smoothly (16). Thus, at larger separations we expect an overall attractive interaction between CS planes.

From an experimental point of view, these results are significant when considering the growth of a second CS plane near to one isolated initial CS plane, and to a first approximation the nucleation of a new CS plane on the edge of an existing group of CS planes. The most favorable nucleation site in terms of elastic strain will be that which results in the minimum interaction energy. This is reflected in the value of α. If α is near to 1.0 pairs of CS planes should not form, but instead rather isolated CS planes. At the other extreme, if α is less than about 0.50, a second CS plane should nucleate as near to the initial CS plane as possible. The actual distance involved will depend upon other factors such as electrostatic interactions. For high values of α the preferential nucleation site will correspond to the minimum in Fig. 9. The n values of the minimum fall in the approximate range 20 to 26 for our data. This corresponds to a CS plane spacing of about 7.4 to 9.7 nm. Thus we can say that if pairs or groups of CS planes with CS plane spacings of less than about 10 nm occur frequently, the material behaves as if α were less than 1.0, and the closer the CS planes lie to each other, the smaller is the effective value of α.

Experimental evidence to test this is limited as the only material to support low concentrations of {001} CS planes is NbO_2F. There are three sets of observations which are relevant here. First it is known that if NbO_2F is heated in sealed tubes together with Nb_3O_7F, no reaction appears to take place (11). That is, the stable phase assembly for substoichiometric NbO_2F is $NbO_2F + Nb_3O_7F$. Nb_3O_7F is the member of the homologous series with $n = 3$, and contains an ordered array of {001} CS planes with a separation of about 0.95 nm. This suggests that under these conditions α is low. However, this evidence is not conclusive as the starting products were NbO_2F and Nb_3O_7F, and the equilibrium products expected are best discussed in terms of the energy of an array of CS planes. This is taken up later.

A second set of experiments are those in which NbO_2F is reduced gradually, as such a procedure is more likely to reveal the interactions between relatively isolated *CS* planes. The earliest structural observations of this phenomenon were by Bursill and Hyde (*10*), who studied the decomposition of NbO_2F crystals under the influence of the electron beam of an electron microscope. We have repeated these observations and found that the crystals decomposed exactly as these latter authors reported. On heating in the electron beam *CS* planes grow into the crystal. They lie upon all {001} planes. Figure 10 shows a typical example. As far as can be judged, the *CS* planes form at random, and closely spaced pairs of *CS* planes occur fairly frequently, as illustrated in Fig. 10. This again suggests that α has rather a low value in this material.

The interpretation of these results in this way is open to some criticism. The beam heating process is fast and the reduction takes place in less than 2 or 3 sec, and often in fractions of a second. In addition, when the intensity of the electron beam is reduced the reaction stops abruptly. The growth conditions are therefore far from equilibrium and unlikely to mirror the energy values calculated here, which pertain to equilibrium situations. Thus the nucleation of a pair or group of *CS* planes may be more indicative of a preferential nucleation site rather than an interaction such as we have postulated. Nevertheless there is no positive evidence for a high value of α in NbO_2F and the supposition that α is low seems reasonable.

The value of α: Ordered Arrays of CS Planes

Two systems support arrays of {001} *CS* planes, the $Nb_2O_5-WO_3$ system, which also makes use of other *CS* plane types, and the niobium oxyfluorides related to NbO_2F. These latter contain only {001} *CS* planes. Let us consider first these niobium oxyfluorides. In equilibrium conditions,
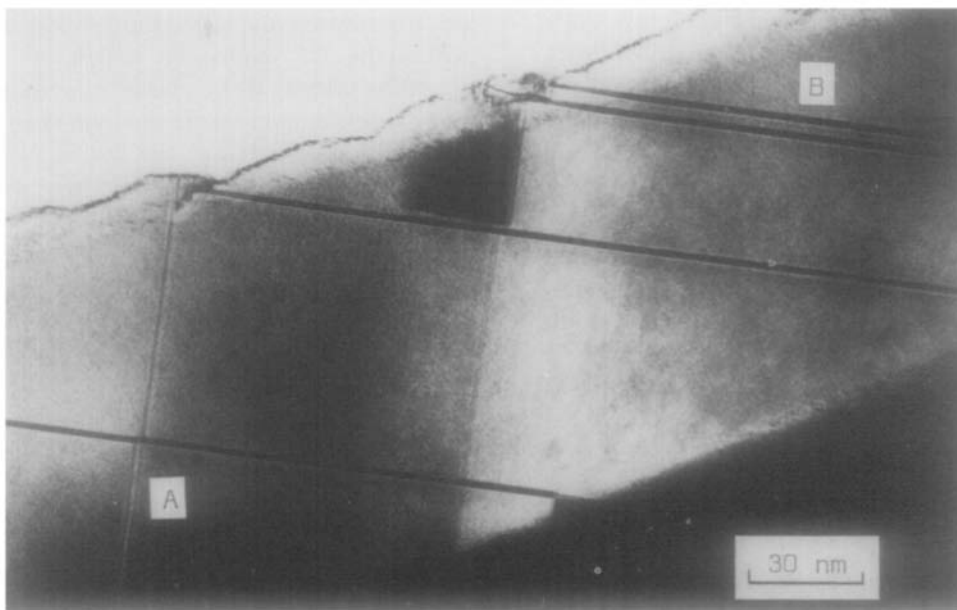

FIG. 10. Electron micrograph of a fragment of an NbO_2F crystal. The prominent dark straight lines are *CS* planes which have grown into the crystal due to the influence of the electron beam. Two pairs of *CS* planes are seen with spacings equivalent to $n = 3$ (marked A) and $n = 11$ (marked B).

reduction of NbO_2F leads directly to the formation of Nb_3O_7F, the $n = 3$ homolog of the M_nX_{3n-1} series based upon ordered {001} CS arrays. Attempts to prepare other n value homologs by heating mixtures of NbO_2F and Nb_3O_7F in sealed platinum capsules, where equilibrium would be likely, resulted in no reaction (11). This shows that the lowest free energy in the system corresponds to the situation in which NbO_2F coexists with the $n = 3$ member of the homologous series. A consideration of Fig. 9 suggests that such a result could hold for any value of α, except $\alpha = 1.0$, for if we take the curves in Fig. 9 to represent the net energy change in disproportionation of a hypothetical homolog $Nb_n(O, F)_{3n-1}$ into NbO_2F and Nb_3O_7F, we can see that the low energy of the $n = 3$ phase will dominate the reaction. This energy difference becomes more pronounced for increasing values of α, but the peak in the high α curves suggest that other homologs should form at least in a metastable form if α was high. The results are therefore somewhat biased toward a low value for α in NbO_2F.

Further information on arrays of {001} CS planes is available if the Nb_2O_5–WO_3 system is considered. Allpress (12) examined samples which had been heated for up to 70 hr at temperatures between 1552 and 1628°K and found n values of 14, 15, and 16 but nothing lower. We have also examined Nb_2O_5–WO_3 samples which have been heated for up to 20 days at 1623 or 1600°K (18). A large number of fragments have been examined, and the only n values found were 10, 11, 12, and 13 except for one fragment in which n was equal to 8. In a number of these samples, the {001} CS phases coexisted with tetragonal tungsten bronze structure phases which form at overall compositions below about $0.25\ Nb_2O_5$: $0.75\ WO_3$. These results suggest that the energy of the CS systems increases appreciably as n falls and that for n values below about 10 rearrangement to the tetragonal tungsten bronze type is ener-

getically favorable. While a large number of factors will be involved in the relative free energies of these phases, our previous considerations suggest that elastic strain energy is significant. In this case, the results in the Nb_2O_3–WO_3 system are more in accord with a value of α close to 1.0, for here the rising curve shown in Fig. 9 implies a sharp rise in elastic strain energy as n falls which is not found in the curves with lower values of α. Our results therefore suggest that the value of α appropriate to WO_3 doped with Nb_2O_5 is close to 1.0.

The Value of α: Chemical Relevance

The experimental data presented suggest that the value of α is likely to vary considerably from one material to another. In the present case α for NbO_2F would seem to be rather low, while for WO_3 doped with a few mole% Nb_2O_5 it would appear to be much nearer to 1.0.

Physically, the value of α is related to the distance that the forces within a CS plane can be transmitted through the crystal both within the CS plane and within the surrounding matrix. If the crystal is considered to be a continuous elastic medium then it is generally assumed that the forces can be transmitted perfectly. That is, the forces originating in any CS plane are effectively influencing the whole of the crystal and there is no decay or damping of the forces at all. In this case the value of the parameter α is taken as 1.0. At the other extreme, we can assume that the forces do not persist at long ranges in the crystal and that their effect is felt only upon nearest neighbors. In such a case each CS plane is only influencing the local microstructure of the crystal in the immediate vicinity of the CS plane and long-range forces do not occur. In this case the permeability of the forces in the structure is low, and in the limit is zero. This corresponds to $\alpha = 0$ in our calculations.

Chemically these concepts can be approximated to the degree of ionicity of the structure and especially the ionicity of the *CS* planes. On the one hand, an elastic continuum implies a structure in which covalent or metallic bonding occurs and the effect of localized atoms or ions is hardly felt. This corresponds to $\alpha = 1.0$. If α is low we are dealing with a situation in which we have discrete atoms or ions and the crystal possesses only little resemblance to a continuous medium. The results we have obtained for α are in good accord with this simple viewpoint. The fluorides are generally regarded as being more ionic than the oxides, and one would expect NbO_2F to be more ionic than WO_3. One would thus expect α for NbO_2F to be lower than for WO_3 or the WO_3 matrix doped with Nb_2O_5. Furthermore, experimental evidence concerning the bond structure of WO_3 (*19*) suggests that an ionic model for this material involving W^{6+} ions is far from the truth and that a covalent model is likely to be a more reasonable description of bonding in WO_3. This agrees well with the high value of α estimated for the Nb_2O_5–WO_3 *CS* phases.

The Value of α: The Case if $\alpha = 1.0$

The results above suggest that in some materials, including WO_3, the approximation that $\alpha = 1.0$ can be quite reasonable. If we take $\alpha = 1.0$, we can treat the *CS* plane itself as a continuous medium, as well as the matrix between the *CS* planes. This allows us to treat the forces within the *CS* planes, and their interactions with each other within the *CS* planes, by means of classical elasticity theory using the compact and elegant Fourier transform technique employed by Stoneham and Durham (*9*) and Shimizu and Iguchi (*15*). This allows us not only to evaluate the U_S and U_R terms given here but also the U_{self} term of Iguchi and Tilley (*5*) which represents the internal energy of the *CS* planes rather than their interaction energies. We have made these calculations for a

number of $\{10m\}$ *CS* planes in an idealized WO_3 type of structure. The results will be presented in a further communication.

The Microstructures of $\{001\}$ CS Phases

In previous reports (*5, 17*) we have used the elastic strain energy calculations to explain a number of features of the microstructures of especially reduced tungsten trioxide. Three situations have been discussed; the nucleation of a new *CS* plane near to another *CS* plane, the nucleation of a new *CS* plane in an array of *CS* planes, and the relative stabilities of various members of homologous series of oxides. In each case it was assumed that the desirable microstructure corresponded to the lowest elastic strain energy, and where several possible microstructures were conceivable the one which was found in practice was that which corresponded to the lowest overall elastic strain energy. Good agreement was found between experimental results and the theoretical predictions.

In the present paper we have already discussed the nucleation of *CS* plane pairs earlier and used this to estimate a value of the parameter α for NbO_2F. We could readily use the data presented here to assess the effect of elastic strain on the other aspects of the microstructures of crystals, namely, the nucleation of new *CS* planes within existing *CS* plane arrays or the stability of homologs in the series M_nX_{3n-1}. However, despite a variety of experimental attempts, no experimental results could be gathered on either of these points. At this stage therefore it seemed fruitless to pursue the theoretical calculations in greater detail.

Acknowledgments

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