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Strain Energy between Parallel {001} Crystallographic Shear Planes in the Tungsten Trioxide Structure

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In order to clarify the appropriateness of the proposal of Iguchi and Tilley, in which the force between two parallel crystallographic shear (*CS*) planes at low separations is an attractive one and, at high separations, a repulsive one, the strain energy between {001} *CS* planes was calculated as a function of the separation. The strain energy was presumed to be due to the forces acting on cations in the *CS* planes and was calculated by using classical elasticity theory by way of the elastic Green's function. The result obtained is in agreement with the original proposal but the *CS* plane separation at which the force between them changes from an attractive to a repulsive one is much larger than was estimated previously. The strain-energy curve has, in addition, a plateau where the interaction of the paired *CS* planes is likely to be in the metastable state. The difference between other related results and ours is discussed in terms of the difference of the model employed.

Introduction

It has been established for several years that reduction of WO_3 crystals to compositions down to approximately $WO_{2.85}$ at temperatures over about 1000°K results in the formation of the crystallographic shear (*CS*) planes in the matrix of the parent oxides (*1–9*). In addition, when reduction is achieved by reaction with certain lower-valent metals, notably Ti, Nb, Ta or Mo, *CS* planes are also formed (*10–13*).

Thus a great deal of precise information on the crystal chemistry of these *CS* structures is available, but quantitative analyses of these phenomena on the basis of solid state physics were started only a few years ago (*14–17*). To this end, it is necessary to consider all of the factors which contribute to the free energy of a crystal containing *CS* planes. As a *CS* plane is one of the extended planar defects, the strain energy of the ions in the matrix due to *CS* planes must be one of the most important terms in free energy, as Anderson suggested (*18*). Stoneham and Durham (*14*) and Iguchi and Tilley (*15*) calculated parts of this term and the results of the latter were in fairly good agreement with the experimental results. Iguchi and Tilley evaluated the strain energy of the matrix between two parallel *CS* planes, which is denoted $(U_s)_2$, and found that the calculated strain energy increases as the increase in the separation between *CS* planes, although the curve is not a smooth one but consists of a series of peaks and valleys when two *CS* planes are close except in the case of the {001} *CS* planes. They also evaluated the strain energy of the matrix due to an isolated *CS* plane, denoted $2(U_s)_1$, where $(U_s)_1$ indicates the strain energy in the matrix of the right- or left-hand side of the isolated *CS* plane, and found that $2(U_s)_1$ is smaller in value than $(U_s)_2$ of the paired *CS* planes at high separations. Referring to this result, they proposed that the $(U_s)_2$ curve should pass through a maximum value and, then, it should fall to $2(U_s)_1$ as the *CS* separation increases to infinity; that is, this behavior may be considered to give rise to a

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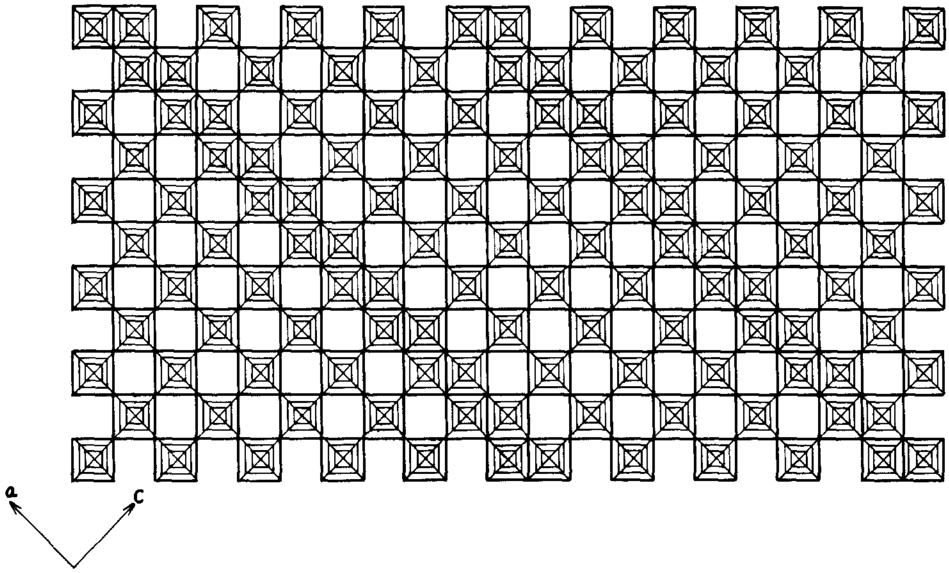

FIG. 1. Idealized representation of a pair of {001} *CS* planes. The *n* value of this pair is 5. The shaded squares represent (WO_6) octahedra. The crystal axes, *a* and *c* axes, are indicated.

virtual attractive force between *CS* planes at low separations, and to a virtual repulsive one between them at high separations. However, they could not justify their proposal completely because their calculations were not, in the main, taken far enough.

In this report, we show that this suggestion is justified by computing $(U_s)_2$ as a function of *CS* plane separation for {001} *CS* pairs, the calculation of which is expected to be the simplest one.

Theory

The cubic form of WO_3 with ReO_3 (DO_9) structure is, in a strict sense, never achieved in the W–O binary system (*19–22*), but we approximate the crystal structure of WO_3 to this idealized ReO_3-type cubic structure in the present theoretical treatment. In this report, we calculate the strain energy of the matrix between two parallel {001} *CS*[1] planes which are introduced into a perfect large single WO_3 crystal, as shown in Fig. 1, and also the strain energy due to an isolated {001} *CS* plane.

Although the distribution of ions in *CS* planes differs from that in the idealized crystal, the separation between anions is the same in both of them. However, the spacing between cations in *CS* planes reduces to about 71% of that in the idealized structure. So, a strong central repulsive force between cations in *CS* planes can be expected. Then, in calculating the strain energy, we have hypothesized the forces, *f*, between cations in *CS* planes as shown in Fig. 2 by a method similar to that in our previous work (*15, 17*). The appropriateness of this hypothesis is justified by the result of De Angelis and Schiavello (*23*) obtained by the method of X-ray photoelectron spectroscopy. In addition, Iguchi (*17*) estimated the magnitude of *f* to be ~ 7.8 $(eV/Å^3) = 1.25 \times 10^{-15} J \cdot nm^{-3}$ by quantifying the displacements of nonparallel {102} *CS* planes in reduced WO_3 obtained by electron microscopy with the theory of elasticity for an isotropic continuum.

In order to calculate the strain energy in this report, we have also assumed that the crystal

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[1] Throughout this paper, the indices of *CS* planes and crystal planes will be referred to the idealized cubic WO_3 cell of the DO_9 (ReO_3) type.

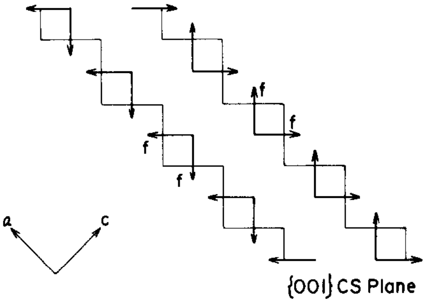

FIG. 2. The direction of the forces assumed to be present within a {001} *CS* plane and which result in elastic strain energy of the surrounding matrix.

can be treated as an isotropic continuum except in the region of *CS* planes which are considered as containing discrete ions. According to Hirth and Lothe (*24*), when a point force, **F**, is applied to the initial point, the displacement of the point which is located at **r** from the initial point, **u**, is represented by

$$\mathbf{u} = \mathbf{G} \cdot \mathbf{F}, \tag{1}$$

where **G** is the elastic Green's function, the *ij*th component of which has the form

$$G_{ij} = (1/8\pi\mu)\left(\delta_{ij}\nabla^2 \mathbf{r} - \frac{\lambda+\mu}{\lambda+2\mu}\frac{\alpha^2 r}{\alpha x_i\, \alpha x_j}\right). \tag{2}$$

As the ReO_3-type crystal has cubic symmetry, we have the following relation among λ (the Lamé constant), μ (the shear modulus), and the elastic constants C_{11}, C_{12}, C_{44},

$$\mu = C_{44} = (C_{11} - C_{12})/2,$$
$$\lambda = C_{12}. \tag{3}$$

Using this theory, we can have the *l*th component of the displacement of the *I*th ion due to a force which is acting on *j*th cation in a *CS* plane, $^I(u_l)_j$. Then, if the *I*th ion is in the matrix between two parallel {001} *CS* planes, 1 and 2, the displacement of this ion along the *l*th direction, $^I u_l$, can be expressed, as described in our previous paper (*15*), by

$${}^I u_l = \sum_j^1 ({}^I u_l)_j + \sum_{j'}^2 ({}^I u_l)_{j'}, \tag{4}$$

where $\sum_j^1$ means the summation of the *l*th component of the displacement due to all cations in *CS* plane 1 and $\sum_{j'}^2$ means a similar summation over all cations in *CS* plane 2. On the other hand, the *kl*th component of the strain, e_{kl}, is related to the component of the displacements by the equation

$$e_{kl} = (\alpha u_k/\alpha x_l + \alpha u_l/\alpha x_k)/2 \tag{5}$$

Referring to Eqs. (4) and (5), the *kl*th component of the strain of the *I*th ion, $^I e_{kl}$, is given by

$${}^I e_{kl} = \sum_j^1 ({}^I e_{kl})_j + \sum_{j'}^2 ({}^I e_{kl})_{j'}, \tag{6}$$

where $({}^I e_{kl})_j$ indicates the *kl*th component of the strain of the *I*th ion due to the *j*th cation in *CS* plane 1 and $({}^I e_{kl})_{j'}$ has a similar meaning. Then we can obtain the strain energy density of the *I*th ion, w_I, by substituting Eq. (6) into Eq. (7):

$$w_I = (\lambda + 2\mu)\left(\sum_{i=1}^3 {}^I e_{ii}\right)^2/2$$
$$+ \mu\left[\sum_{i,j=1}^3 ({}^I e_{ij})^2 - \sum_{i,j=1}^3 ({}^I e_{ii})({}^I e_{jj})\right], \tag{7}$$

where $i \neq j$.

When an isolated *CS* plane is introduced into a single WO_3 crystal, the displacement and the strain of the *I*th ion are given by

$${}^I u_l = \sum_j^1 ({}^I u_l)_j, \tag{8a}$$

$${}^I e_{kl} = \sum_j^1 ({}^I e_{kl})_j. \tag{8b}$$

The strain energy of the *I*th ion due to an isolated *CS* plane can be obtained in a similar way.

Calculation and Results

We must calculate the strain energy of each ion in the matrix due to the *CS* planes. In this

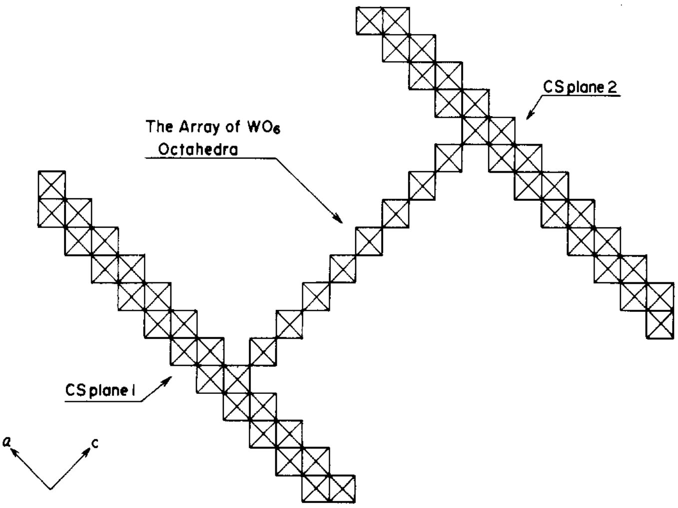

FIG. 3. The array of WO_6 octahedra which bridges the centers of the *CS* planes, 1 and 2. The *n* value of this array is 10.

calculation, we have used the same ratios of the elastic constants C_{11}, C_{12}, and C_{44} as Stoneham and Durham (*14*), i.e.,

$$C_{11}:C_{12}:C_{44} = 16:7:5.$$

In order to evaluate the values of Eq. (6) or Eq. (8b), the strain of each ion in the matrix should ideally be the summation of the strains due to all cations in the *CS* planes, but this is clearly impractical. So, we have approximated a block of *CS* planes which has a length of $85a$ in the $\langle 100 \rangle$ crystal direction and a height of $41a$ in $\langle 010 \rangle$ as a $\{001\}$ *CS* plane, where a is the unit cell edge of the idealized cubic WO_3, equal to the octahedron diagonal length. We can rely upon this approximation because of the following check. We have calculated the strain energy of the nearest W ion to the center of a block of $87a \times 43a$ due to this block and have compared it with the equivalent value due to a block of $85a \times 41a$. It is found that the absolute ratio of the difference between these values to the strain energy due to a block of $85a \times 41a$ is less than 0.05.

Then, we have computed the strain energy of an array of WO_6 octahedra which combines the centers of the parallel blocks of *CS* planes, 1 and 2, as shown in Fig. 3 as a function of the *n* value which is proportional to the separation between *CS* planes. To do this, we have calculated the strain energies of W ions in this array, SEW, the strain energies of O ions in the mirror plane ($z = 0.0$) of this array, SEO, and the strain energies of O ions in the plane of $z = \pm a/2$ in this array, SEU, by using Eq. (6). For example, SEW is evaluated as follows

$$\mathrm{SEW} = \sum_{i=1}^{n-2} (w_W)_i, \tag{9}$$

where $(w_W)_i$ is the strain energy of the W ion which is the center of the *i*th octahedron in this array which has $(n - 2)$ WO_6 octahedra when the separation between the parallel $\{001\}$ *CS* planes is expressed as *n*.

According to our previous report (*15*), we reduce the strain energy of this array to the value per unit area of *CS* planes, which is denoted as $(U_s)_2$, as

$$(U_s)_2 = (4\pi/3a^2)[r_W^3 \times \mathrm{SEW} + r_O^3 \times (\mathrm{SEO} + \mathrm{SEU})] \tag{10}$$

where r_W and r_O are the ionic radii of O^{2-} and W^{6+} ions and the following values were used (*25*),

$$r_W = 0.60\ \text{Å}$$
$$r_O = 1.40\ \text{Å}.$$

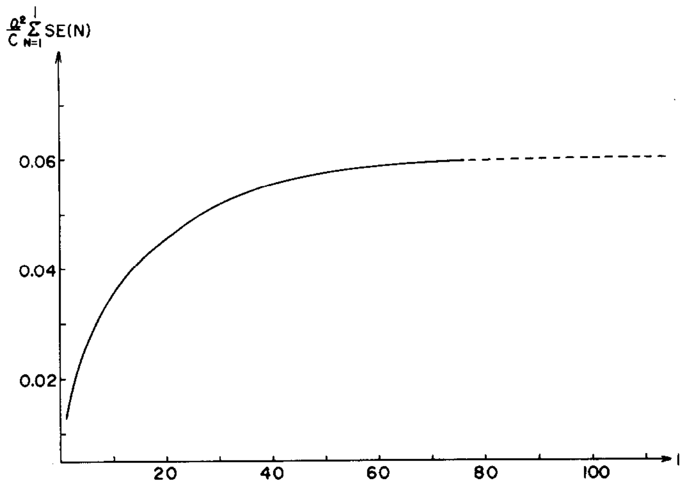

FIG. 4. The elastic strain energy for a single {001} *CS* plane in an idealized WO_3 matrix, $(a^2/C)\sum_{N=1}^{I} SE(N)$, as a function of I, where $SE(N) = [SEO(N) + SEU(N) + (r_w/r_0)^3\, SEW(N)]$ and $C = (\lambda + 2\mu)\,(f/8\pi\mu)^2(4\pi r_0^3/3)$. The broken line represents the extrapolated values as I becomes large.

Moreover, we have calculated the strain energy of the matrix due to an isolated {001} *CS* plane per unit area of the *CS* plane, $2(U_s)_1$. By a method similar to the calculation in the *CS* pair, we have computed the strain energy of an array of WO_6 octahedra which extends to infinity from the center of the block of $85a \times 41a$, perpendicular to this block. We denote the strain energy of the W ion in the Nth octahedron as SEW(N) and the strain energies of the O ions in the mirror plane ($z = 0.0$) and in the plane of $z = \pm a/2$ of the Nth octahedron as SEO(N) and SEU(N), respectively; then $2(U_s)_1$ can be represented by

$$2(U_s)_1 = 2(4\pi/3a^2) \sum_{N=1}^{\infty} [r_W^3 \times SEW(N) + r_O^3 \times (SEO(N) + SEU(N))]. \qquad (11)$$

In Fig. 4, the values of $\sum_{N=1}^{I}$ [SEO(N) + SEU(N) + $(r_w/r_o)^3$ × SEW(N)] have been plotted as a function of I. The extrapolated value of $\sum_{N=1}^{I}$ [SEO(N) + SEU(N) + $(r_w/r_o)^3$ × SEW(N)] at $I = \infty$ is proportional to $(U_s)_1$.

In Fig. 5, we have shown the relation of $(U_s)_2$ and n and we have plotted $2(U_s)_1$, which is extrapolated in Fig. 4, as $(U_s)_2$ at $n = \infty$, because the strain energy in the matrix between the two *CS* planes which are separated infinitely is to be $2(U_s)_1$. In Figs. 4 and 5, the vertical axes are represented in units of C/a^2, where $C = (\lambda + 2\mu)(f/8\pi\mu)^2(4\pi r_0{}^3/3)$. In our previous paper (*15*), we calculated $(U_s)_1$ and $(U_s)_2$ of {001} *CS* planes in a similar fashion, but the array of WO_6 octahedra was not normal to the block of *CS* planes. Therefore, the values of $(U_s)_1$ and $(U_s)_2$ obtained earlier differ slightly from the values in this report.

Discussion

A. Thermodynamics

According to Tilley (*26*), the free energy of reduced crystal $WO_{3-x}(c, CS)$ containing *CS* planes can be expressed as

$$G(N,N_d,T) = G_0(N) + G_d(N,N) + G_l(N_d). \quad (12)$$

In this equation, G_0 is the free energy of the original (perfect) WO_3 crystal before reduction and which contains N tungsten ions, G_d is the

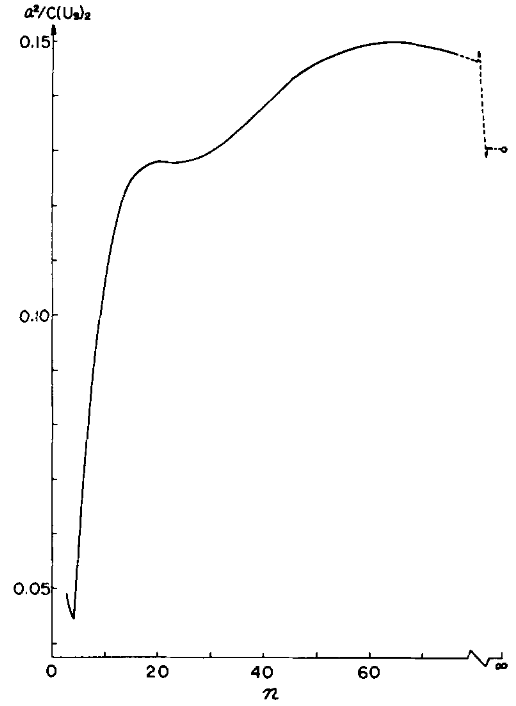

FIG. 5. The elastic strain energy between two parallel {001} *CS* planes, $(a^2/C)(U_s)_2$, plotted as a function of the number of octahedra, n, between them. The extrapolated curve at $n > 76$ is plotted by a broken line. The plot at $n = \infty$ is the extrapolated value of $(a^2/C)\sum_{N=1}^{l} \mathrm{SE}(N)$ at $l = \infty$ in Fig. 4.

free energy of the $N_d CS$ planes introduced as a result of the reduction, and G_i is a free-energy contribution resulting from all the interactions between the *CS* planes and their surroundings. So the strain energy calculated above belongs to G_i.

The model employed in this work is the same model as that described in our previous papers (*15, 17*). Thus, the free-energy change due to a *CS* plane introduced into a perfect crystal, ΔG_1, can be given by the equation

$$\Delta G_1 = (U_d) + (U_{\mathrm{self}}) + \gamma + 2(U_s)_1 + 2(U_e)_1. \tag{13}$$

The formation of *CS* planes needs the dissociation of oxygen atoms from the crystal and we denote the change in the free energy associated with this reaction as (U_d). The term (U_{self}) represents the elastic strain energy of the *CS* plane, itself. So, (U_{self}) is considered to be the eigenvalue of the *CS* plane in our model. As described in the Introduction, $2(U_s)_1$ is the strain energy in the matrix due to the isolated *CS* plane and $2(U_e)_1$ is the electrostatic interaction energy among the ions in the *CS* plane and surrounding ions. The term γ is the interface energy between a *CS* plane and the surrounding matrix, which occurs in Eq. (13) because the difference in physical and chemical properties between the *CS* regions and the matrix is expected.

In the similar way, we can express the free-energy change due to a pair of *CS* planes introduced into a perfect crystal, ΔG_2, as

$$\Delta G_2 = 2(U_d) + 2(U_{\mathrm{self}}) + 2\gamma + 2(U_s)_1 + (U_s)_2 + 2(U_e)_1 + (U_e)_2 + (U_{\mathrm{rep}}), \tag{14}$$

where $(U_e)_2$ is the electrostatic interaction energy among the ions in the *CS* planes and the ions in the matrix between the *CS* pair, and (U_{rep}) represents the repulsive coulomb energy between the *CS* planes.

Therefore, (U_d) and (U_{self}) belong to G_d, and other terms in Eqs. (13) and (14) belong to G_i. Unfortunately, to date we do not have any information relating to the electronic states in the *CS* planes from either experiment or theory, so we have assumed the *CS* planes to be neutral. If the *CS* planes are neutral, Eq. (14) can be expressed approximately as follows

$$\Delta G_2 \simeq 2(U_d) + 2(U_{\mathrm{self}}) + 2\gamma + 2(U_s)_1 + (U_s)_2. \tag{14'}$$

Among these terms, only $(U_s)_2$ varies with the separation between the *CS* planes, and the others are constant terms. Therefore, we can see the relation of ΔG_2 and the spacing between the *CS* pair by plotting $(U_s)_2$ as a function of n.

B. Interaction between Two Parallel {001} *CS* Planes

As described above, the curve in Fig. 5 is considered to represent the relation of ΔG_2 and *n*. According to this result, ΔG_2 decreases as *n* increases from 3 to 4 and in the region of $n =$ 4 to 18, ΔG_2 increases smoothly as *n* increases. This curve has a plateau between $n = 19$ and 25, but ΔG_2 increases very slightly in this region except at $n = 22$, where ΔG_2 has a minimum which is not obvious in Fig. 5. Then, ΔG_2 increases again as *n* increases from 26 to 63, after which ΔG_2 decreases smoothly to the value of $2(U_s)_1$ as *n* increases. This behavior shows that there is an attractive force between two parallel {001} *CS* planes in the region of $n = 4$ to 63 except at $n = 22$ and the force between the *CS* pair is a repulsive one when *n* is over 64. Thus, the force of the *CS* pair varies with its distance in a fashion similar to that between two edge dislocations of the same sign (*27*). However, it is not certain whether the energy changes involved would be sufficient to cause the *CS* planes to move in a crystal, as the ionic mobility necessary is dependent on a large number of factors. In the plateau, these two *CS* planes are in a metastable state.

In Fig. 6, we have shown the force between the *CS* planes as a function of *n*, which is obtained approximately as follows

$$\begin{aligned}(F)_{n=n_i} &\propto -(\alpha\Delta G_2/\alpha n)_{n=ni}\\ &\simeq -[\Delta G_2(n_i) - \Delta G_2(n_i+1)]/[n_i-(n_i+1)]\\ &= \Delta G_2(n_i) - \Delta G_2(n_i+1), \qquad (15)\end{aligned}$$

where $(F)_{n=ni}$ and $\Delta G_2(n_i)$ represent the force and the free-energy change between the two *CS* planes at $n = n_i$.

As seen in Figs. 5 and 6, two parallel {001} *CS* planes at low separations attract each other strongly and especially in the region of $n = 4$ to 18, these *CS* planes tend to be as close as possible. However, at very small separations, they repel each other (see the $(U_s)_2$ curve at $n = 3$ and 4).

In order to understand the reason why the curve of ΔG_2 vs *n* has such a plateau, we have shown SEW, SEO, and SEU in Eq. (10) as a function of *n* in Fig. 7. It is found that the curve of SEU vs *n* has two peaks, at $n = 15$ and 63, and one minimum, at $n = 28$, and the

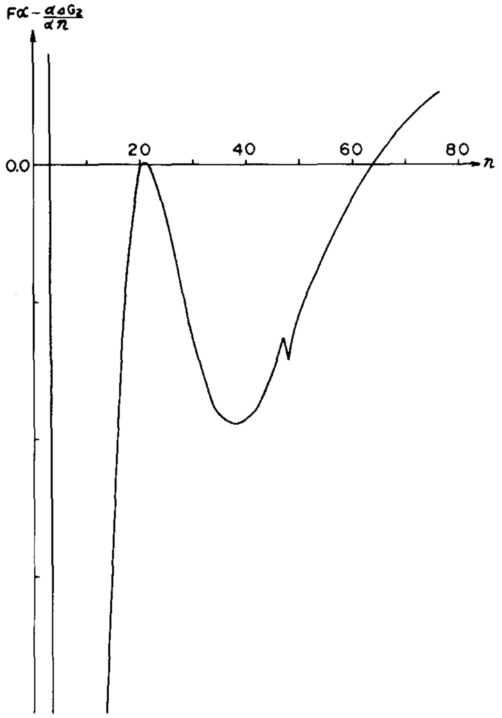

FIG. 6. The forces between two parallel {001} *CS* planes as a function of the *n* value. The force is plotted in arbitrary units.

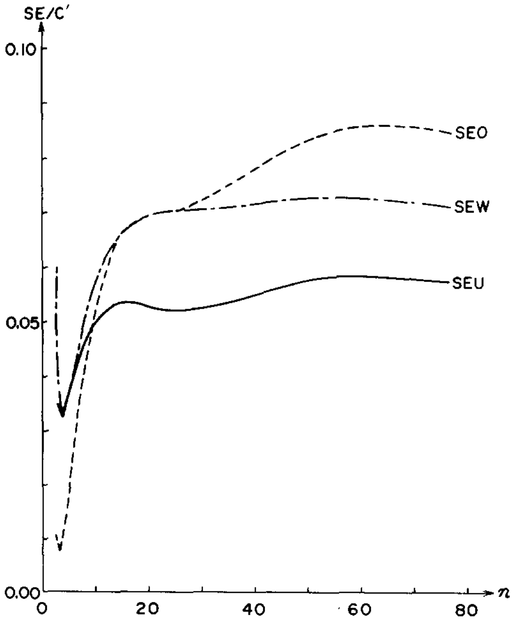

FIG. 7. The relations of SEW, SEO, and SEU vs *n*. The values, SE, of SEW, SEO, and SEU are plotted in units of SE/C′, where $C' = (\lambda + 2\mu)(f/8\pi\mu)$.

increasing rate of SEO decreases in the region of $n = 20$ to 26. Referring to these results, the curve of ΔG_2 vs n seems very sensitive to the curves of SEU and SEO, which are considered to give rise the plateau. In a previous report by Iguchi and Tilley (*15*), the strain energy, $(U_s)_2$, between two parallel {102} *CS* planes in the region of $n = 6$ to 34 was calculated in a similar way and it was found that $(U_s)_2$ has a peak at $n = 33$. So, they anticipated that $(U_s)_2$ would decrease as n increased beyond 34 in this system. However, the result in this report indicates that this conclusion may be slightly wrong and the decrease in $(U_s)_2$ associated with the increase in n from 33 to 34 may be that corresponding to the minimum of the curve in Fig. 5. According to the Iguchi–Tilley calculation on the {001} *CS* pair between $n =$ 3 to 17, the $(U_s)_2$ curve is quite similar to the result in this report and nearly flat at $n \simeq 17$. So, they estimated that the maximum point of the $(U_s)_2$ curve would be close to $n = 17$, but this is also wrong. The *CS* plane separations at which the maximum points of $(U_s)_2$ take place are much larger than they expected.

Not only in the Nb–W–O (*12*) and the Ti–W–O (*13*) ternary systems, but also in the niobium oxide fluorides (ReO_3-type crystals), when beam heated in the electron microscope (*6, 28–31*), {001} *CS* planes are formed. In the Nb–W–O and Ti–W–O systems, quasi-ordered or ordered arrays of {001} *CS* planes are formed, but in the niobium oxide fluorides, pairs of {001} *CS* planes are observed. A careful statistical survey of experimental results equivalent to that for the {103} *CS* planes shown in the previous work (*15*) would be very helpful for a discussion of the correlation between the calculations in this report and the experimental results.

The results in this report suggest that, except in the case of the quite small concentration of {001} *CS* planes, they would tend to cluster in pairs or in groups. Besides the strain energy, however, there still remain other factors which would contribute to the interaction between *CS* planes—for example, the lattice polarization, the lattice relaxation, and so on—but the theoretical treatments for these terms are not yet established, so they will be postponed to the future.

C. Comparison with the Result of Stoneham and Durham

Stoneham and Durham (*14*) also investigated the interaction between the parallel {001} *CS* planes, but their result is quite different from ours. This difference is ascribed to the difference between their model and ours. They, using the Fourier space, calculated the strain energy of each ion in one *CS* plane which was obtained by the scalar product of the force acting on the ion with the displacement of that ion induced by all the ions in the other *CS* plane, and they defined the strain energy between the two *CS* planes as the summation of the strain energies of all ions in the *CS* planes. So, in their model, the matrix between the *CS* planes plays the role of the medium which transmits the force from one *CS* plane to the other and the regions of the *CS* planes are considered to be the isotropic continua as well as the matrix. The strain energy obtained by them is, therefore, the one due to the *CS* plane itself, which is considered to belong to (U_{self}) in this report. On the other hand, in our model, the region of the *CS* plane is not a continuum and the value of (U_{self}) is free from surrounding *CS* planes.

At present, it is impossible to say which strain energy is more important. It is to be the subject of a further publication to clarify this point.

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