

## The Electrostatic Interaction Energy between Crystallographic Shear Planes in Reduced Tungsten Trioxide

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The contribution to the internal energy of slightly reduced  $\text{WO}_3$  crystals containing *CS* planes due to electrostatic interactions between ions in the *CS* plane and ions in the surrounding crystal matrix or in neighboring *CS* planes has been investigated theoretically. Three *CS* plane geometries have been studied,  $\{102\}$ ,  $\{103\}$ , and  $\{001\}$ . Using simple assumptions about the charge distribution in the *CS* planes, numerical values for these interaction energies have been estimated. It was found that the interaction energy between a *CS* plane and the surrounding matrix was negligible compared to the repulsive (coulomb) interaction energy between a pair of *CS* planes. The magnitude of this repulsive energy was in the order  $\{103\} < \{102\} < \{001\}$ . The possible significance of these results in controlling the microstructure of crystals containing *CS* planes is discussed.

### Introduction

It has been known for some years now that the loss of oxygen from  $\text{WO}_3$  crystals results in the formation of crystallographic shear (*CS*) planes in the matrix of the parent oxide. Initially these *CS* planes are distributed at random and lie on  $\{102\}$  planes (referred to an idealized cubic  $\text{ReO}_3$  type unit cell). As the degree of reduction increases, the *CS* plane density increases to result in fairly well-ordered arrays of  $\{102\}$  *CS* planes. When the overall reduction of the crystals falls below about  $\text{WO}_{2.93}$ , the *CS* planes lie upon  $\{103\}$  planes rather than  $\{102\}$  planes, and form quasi-ordered arrays. In  $\text{WO}_3$  doped with other metals, other *CS* plane indices are also found, namely,  $\{104\}$  and  $\{001\}$ , and in such cases the order of reduction is  $\{102\} \rightarrow \{103\} \rightarrow \{104\} \rightarrow \{001\}$ . The structural geometry of these oxides is described fully in a number of recent reviews (1-3) and therefore will not be described further here except in such detail as is needed.

From the first discovery of these oxides there has been interest and speculation concerning both the mechanisms of formation of *CS* planes in  $\text{WO}_3$  and on the forces between *CS* planes which allow them to order into regular or fairly regular arrays. As far as the inter-*CS* plane forces are concerned speculative discussions (see, e.g., (4)) have centered upon elastic strain energy and coulombic (electrostatic) interactions. An investigation of the elastic strain due to  $\{100\}$  *CS* planes in an idealized  $\text{ReO}_3$  matrix was made by Stoneham and Durham (5) and more extensive calculations of the elastic strain energy due to  $\{102\}$ ,  $\{103\}$ , and  $\{001\}$  *CS* planes in  $\text{WO}_3$  by us (6). This latter paper investigated the proposal that the microstructures occurring in reduced  $\text{WO}_3$  were a consequence of the elastic strain energy due to *CS* planes in the parent oxide and represented situations with lowest values of elastic strain. Although a generally good correlation between microstructure and elastic strain was observed, at low *CS* plane spacings it was found that the elastic strain energy considerations were becoming a less reliable guide and that other factors were of importance. One of these could be electrostatic

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interaction energy. In order to take this suggestion further we have calculated the electrostatic interaction energy due to  $\{102\}$ ,  $\{103\}$ ,

and  $\{001\}$  CS planes in reduced  $\text{WO}_3$ . These results are presented in this communication.

### Theory

The idealized structures of  $\{102\}$ ,  $\{103\}$ , and  $\{001\}$  CS planes, shown in Fig. 1, reveal that the atom density in the CS planes is appreciably higher than in the  $\text{WO}_3$ -like parent matrix. At present, the real charge type and distribution in these oxides is unknown, so for purposes of our calculations we have assumed that the crystals can be treated as ionic, containing  $\text{O}^{2-}$  anions and some or all of the cations  $\text{W}^{6+}$ ,  $\text{W}^{5+}$ , and  $\text{W}^{4+}$ . Using this model it is a straightforward matter to maintain the CS planes as formally neutral over small segments of their length. In order to keep the following equations as general as possible, rather than distribute these ions in arbitrary arrangements, we have chosen to retain the nominal charge on each  $\text{W}^{n+}$  ion as 6+ and to add an arbitrary additional charge to the units comprising the CS plane. In this case the charge per unit of a  $\{102\}$  CS plane is  $(2 + \delta_{102})e$ , of a  $\{103\}$  plane is  $(4 + \delta_{103})e$ , and of a  $\{001\}$  CS plane is  $(2 + \delta_{001})e$ . The units chosen are those shown in Fig. 1, that is, a block of four edge-shared octahedra in the case of  $\{102\}$  CS, a block of six edge-shared octahedra in the case of  $\{103\}$  CS, and a pair of edge-shared octahedra in the case of  $\{001\}$  CS. The value is, of course, not necessarily the same for each CS plane type, and could, in principle, be zero, or greater or less than 2.0.

As the location of any such charges is unknown at present, we have chosen to distribute them statistically, as shown in Fig. 2. That is, in the  $i$ th unit of a  $\{102\}$  CS plane, two  $(2 + \delta_{102})e/2$  charges are accommodated at  $(X_i - \frac{1}{2}, Y_i, Z_i)$  and  $(X_i - \frac{3}{2}, Y_i + 1, Z_i)$ ; similarly, in the  $i$ th unit of a  $\{103\}$  CS plane, three  $(4 + \delta_{103})e/3$  charges are accommodated at  $(X_i - \frac{1}{2}, Y_i, Z_i)$ ,  $(X_i - \frac{3}{2}, Y_i + 1, Z_i)$  and  $(X_i - \frac{5}{2}, Y_i + 2, Z_i)$  and in the  $i$ th unit of a  $\{001\}$  CS plane, a  $(2 + \delta_{001})e$  charge is located at  $(X_i - \frac{1}{2}, Y_i, Z_i)$ , where  $(X_i, Y_i, Z_i)$  is the coordination of the reference position of the  $i$ th unit of each CS plane, as shown in Fig. 2. For simplicity of calculation we have set the

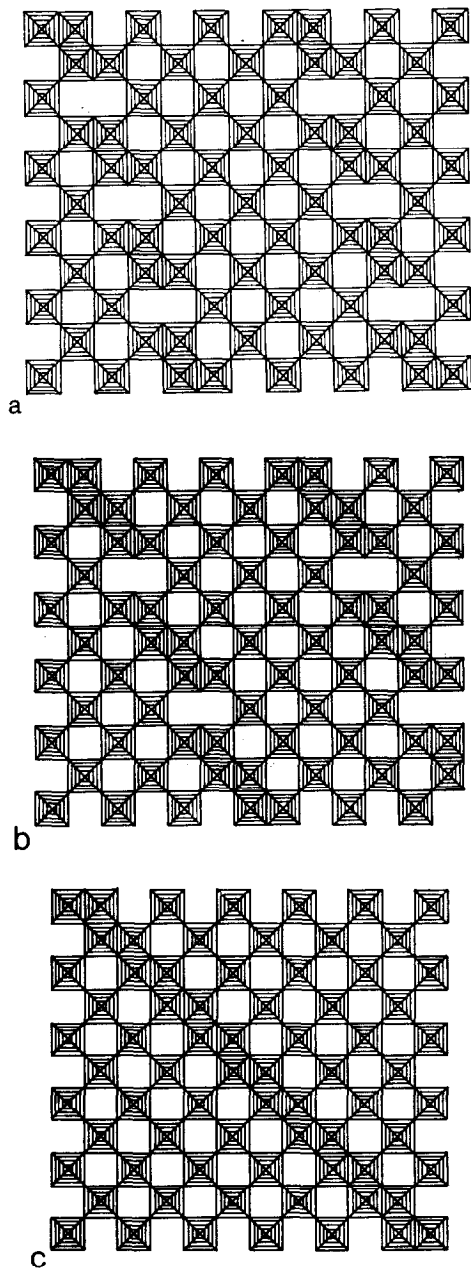


FIG. 1. Idealized projections of the structures of (a)  $\{102\}$  CS planes; (b)  $\{103\}$  CS planes, and (c) a  $\{101\}$  CS plane in an idealized cubic  $\text{WO}_3$  matrix. The shaded squares represent  $(\text{WO}_6)$  octahedra.

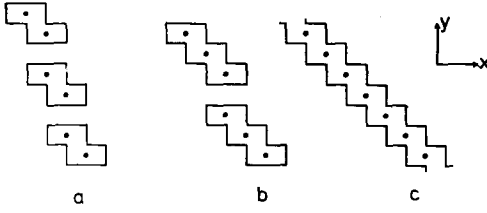


FIG. 2. Schematic illustration of the blocks of edge-sharing octahedra in (a) {102}, (b) {103}, and (c) {001} CS planes. The black circles show the positions of the excess charges in the CS planes used in the calculations,  $\frac{1}{2}(2 + \delta_{102})e$  for (a),  $\frac{1}{3}(4 + \delta_{103})e$  for (b), and  $(2 + \delta_{001})e$  for (c). The coordinate axes used in the calculations are also marked.

coordinate  $x$ -,  $y$ -, and  $z$ -axes as shown in Fig. 2 and we use the length of an idealized octahedron edge,  $a/2^{1/2}$ , as a unit length along each axis, where  $a$  is the unit cell edge of the idealized cubic WO<sub>3</sub>. It should be noted that these axes, which are different from the crystallographic axes, are used only for the purposes of the calculation. All features of crystallographic or morphological interest are referred to the conventional unit cell axes.

When CS planes with these charges are formed in a crystal, the electrostatic interaction energies increase the internal energy by an amount which are designated as  $U_e$ . Three different levels of interaction can be separated, viz.,  $(U_e)_1$ , the interaction energy between a single CS plane and the surrounding matrix;  $(U_e)_2$ , the interaction energy between the crystal matrix lying between two CS planes and these CS planes and, if the CS planes are not in a neutral state,  $(U_e)_{\text{rep}}$ , the repulsive coulomb energy between two nonneutral CS planes.

We can thus write down the total coulomb energy due to an isolated CS plane in a crystal as

$$(U_e)_{\text{isol}} = (U_e)_1, \quad (1)$$

for a pair of CS planes as

$$(U_e)_{\text{pair}} = (U_e)_1 + (U_e)_2 + (U_e)_{\text{rep}}, \quad (2)$$

and for a cluster of  $N$  CS planes as

$$(U_e)_{\text{clust}} = (U_e)_1 + (N-1)(U_e)_2 + (N-1)(U_e)_{\text{rep}}. \quad (3)$$

As described in the previous papers (6, 7), the free energy of a reduced crystal of

WO<sub>3</sub> ( $c$ , CS) containing CS planes can be expressed as

$$G(N, N_d, T) = G_0(N) + G_d(N, N_d) + G_i(N_d), \quad (4)$$

where  $G_0$  represents the free energy of the perfect WO<sub>3</sub> crystal before reduction and containing  $N$  tungsten atoms,  $G_d$  is the free energy due to  $N_d$  noninteracting CS planes and  $G_i$  is the free energy contribution due to all the interactions between the CS planes and each other or the surrounding crystal matrix.  $G_d$  is therefore analogous to a defect formation energy and  $G_i$  to a defect interaction energy. Formally, the terms in  $U_e$  will belong to  $G_i$ .

### 2.1. $(U_e)_1$

For a {103} CS plane, the coulomb interaction energy  $(E_c)_i$  between the  $i$ th WO<sub>6</sub> octahedron, the W ion of which is located at  $(X_i, Y_i, Z_i)$ , and the charges in the  $i$ th unit of the CS plane at a position  $(X_i, Y_i, Z_i)$  (see Fig. 2) has the form

$$(E_c)_i = \left[ \frac{(4 + \delta_{103})}{3} e^2 / \epsilon \right] \times \sum_{n=1}^3 \left\{ \frac{6}{|\mathbf{r}_n|} - \frac{1}{|\mathbf{r}_n + 2/(2)^{1/2}\mathbf{k}|} - \frac{1}{|\mathbf{r}_n - 2/(2)^{1/2}\mathbf{k}|} - \frac{1}{|\mathbf{r}_n + \mathbf{i} + \mathbf{j}|} - \frac{1}{|\mathbf{r}_n + \mathbf{i} - \mathbf{j}|} - \frac{1}{|\mathbf{r}_n - \mathbf{i} - \mathbf{j}|} - \frac{1}{|\mathbf{r}_n - \mathbf{i} + \mathbf{j}|} \right\} \quad (5)$$

where  $\mathbf{i}$ ,  $\mathbf{j}$ ,  $\mathbf{k}$  are the unit vectors along  $x$ -,  $y$ -, and  $z$ -axes and  $\epsilon$  is the dielectric constant of the crystal. Also

$$\begin{aligned} \mathbf{r}_1 &= (X_i - X_i)\mathbf{i} + (Y_i - Y_i)\mathbf{j} \\ &\quad + (Z_i - Z_i)\mathbf{k}, \\ \mathbf{r}_2 &= (X_i - X_i + \frac{3}{2})\mathbf{i} + (Y_i - Y_i - 1) \\ &\quad + (Z_i - Z_i)\mathbf{k}, \\ \mathbf{r}_3 &= (X_i - X_i + \frac{5}{2})\mathbf{i} + (Y_i - Y_i - 2)\mathbf{j} \\ &\quad + (Z_i - Z_i)\mathbf{k}. \end{aligned} \quad (6)$$

As the coulomb interaction energy between the  $i$ th octahedron and all the charges in the {103} CS plane is  $\sum_i (E_c)_i$  where  $\sum_i$  indicates the

summation of the coulomb interaction energy caused by charges in energy unit of the {103} CS plane,  $(U_e)_1$  is given by the following

$$(U_e)_1 = \sum_I \sum_i (E_c)_i, \quad (7)$$

where  $\sum_I$  indicates the summation of the coulomb interaction energy of all surrounding  $\text{WO}_6$  octahedra.

By similar reasoning  $(U_e)_1$  for {102} and {001} CS planes can be obtained.

### 2.2. $(U_e)_2$

Let the  $I$ th octahedron, the center of which is located at  $(X_I, Y_I, Z_I)$ , lie between the {103} CS planes 1 and 2. In this case there are two coulomb forces, one between the  $I$ th octahedron and the charges in the {103} CS plane 1 and the other between the  $I$ th octahedron and charges in the {103} CS plane 2. These coulomb forces increase the internal energy by  $(\sum_i^1 (E_c)_i + \sum_{i'}^2 (E_c)_{i'})$ , where  $(E_c)_{i'}$  denotes the coulomb interaction energy between the  $I$ th octahedron and the charges in the  $i'$ th unit of the {103} CS plane 2,  $(E_c)_i$  is given by Eq. (5) and  $\sum_i^1$  and  $\sum_{i'}^2$  have a similar meaning to that in Eq. (7)

Then,  $(U_e)_2$  has the form,

$$(U_e)_2 = \sum_I^{1,2} \left( \sum_i^1 (E_c)_i + \sum_{i'}^2 (E_c)_{i'} \right), \quad (8)$$

where  $\sum_I^{1,2}$  indicates the summation of the coulomb energies of all octahedra between the CS plane 1 and 2.

By similar methods,  $(U_e)_2$  for {102} and {001} CS planes can be obtained.

### 2.3. $(U_e)_{\text{rep}}$

The repulsive coulomb energy,  $(E_e)_{\text{rep}}$  between two nonneutral {103} CS planes is calculated as follows. The coulomb interaction energy between the excess charge  $(4 + \delta_{103})e$  of the  $i$ th unit in the {103} CS plane 1 and that in the  $i'$ th unit of the CS plane 2,  $(E_{\text{rep}})_{ii'}$ , is given by Eq. (9),

$$(E_{\text{rep}})_{ii'} = [(4 + \delta_{103})^2 e^2 / 9\epsilon] \sum_{j=1}^3 \{ 1/|(\mathbf{r}_{ii'})_j| + 1/|(\mathbf{r}_{ii'})_j - \mathbf{i} + \mathbf{j}| + 1/|(\mathbf{r}_{ii'}) - 2\mathbf{i} + 2\mathbf{j}| \}, \quad (9)$$

where  $(X_i, Y_i, Z_i)$  and  $(X_{i'}, Y_{i'}, Z_{i'})$  are the coordinations of the references position of  $i$ th unit in CS plane 1 and  $i'$ th unit in CS plane 2.

The value of  $(U_e)_{\text{rep}}$  is obtained by summation of all of the coulomb interaction energies between units in CS planes 1 and 2, and we can write  $(U_e)_{\text{rep}}$  in the following way

$$(U_e)_{\text{rep}} = [(4 + \delta_{103})^2 e^2 / 9\epsilon] \sum_i^1 \sum_{i'}^2 (E_{\text{rep}})_{ii'}, \quad (10)$$

where  $\sum_i^1, \sum_{i'}^2$  have the same meaning as those in Eq. (7).

By similar means, we can derive expressions for  $(U_e)_{\text{rep}}$  between {102} or {001} CS planes.

## Calculations and Results

In the calculations described in this report, we have employed the following values:  $a = 0.38$  nm;  $\epsilon = 300$  (8, 9).

### 3.1. $(U_e)_1$ and $(U_e)_2$

For the present purposes the coulomb energies,  $(U_e)_1$  and  $(U_e)_2$ , are defined in the following way. One CS plane is introduced into a single crystal (height  $H$ , width  $W$ )

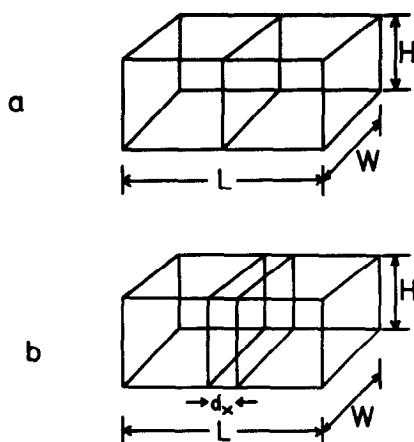


FIG. 3. Schematic illustration of a crystal of  $\text{WO}_3$  containing (a) one CS plane and (b) two CS planes, showing the dimensions used in the calculations.

as shown in Fig. 3 and this CS plane has a coulomb interaction with all surrounding WO<sub>6</sub> octahedra in the crystal. The summation of the coulomb energy of each octahedron in the crystal due to this CS plane is divided by the cross section of the crystal,  $H \times W$ , and this energy per unit area is defined as  $(U_e)_1$ . Similarly, when two CS planes are introduced into the crystal, the summation of the coulomb energies of all octahedra between two CS planes is also divided by the cross section area and it is this value that is defined as  $(U_e)_2$ .

In order to obtain values of  $(U_e)_1$  and  $(U_e)_2$ , we must calculate the coulomb interaction energy between the  $l$ th octahedron and the charges in the unit of CS planes shown in Fig. 2, that is,  $\sum_i (E_c)_i$  or  $\sum_{i'} (E_c)_{i'}$  to start with. It follows from Section 2 that the coulomb interaction energy of each octahedron should ideally be the summation of the coulomb interaction energies due to all of the units in the CS plane. This calculation, however, is impractical, so we have chosen to sum only the coulomb interaction energies due to  $15 \times 30$  units, in the case of a {102} CS plane,  $13 \times 30$  units in the case of a {103} CS plane, and  $41 \times 30$  units in the case of an {001} CS plane. The units which give the largest coulomb interaction energies are, as expected, in the centers of these blocks of units and it was found that the absolute value of the ratio of the coulomb energy due to a unit in the boundary to the coulomb interaction energy due to a unit in the center was less than  $10^{-3}$ . After the calculation of  $\sum_i (E_c)_i$  or  $\sum_{i'} (E_c)_{i'}$  we can obtain the values of  $(U_e)_1$  by using Eq. (7). The steps in this calculation are outlined below. In the case of a {102} CS plane, there are three octahedra parallel to each unit which have their centers at a distance of  $(2N + \frac{1}{2})a/2^{\frac{1}{2}}$  from the center line in each unit, where  $N$  is a positive integer. The average value of the coulomb energies of these three octahedra,  $[E_c(N)]_{av}$ , is related to  $(U_e)_1$  by the following equations.

$$(U_e)_1 = (2(2)^{1/2}/(10)^{1/2}a^2) \sum_{N=1}^{\infty} [E_c(N)]_{av}. \quad (11.1)$$

Similarly, the values of  $(U_e)_1$  for a {103} and a

{001} CS plane are given by

$$(U_e)_1 = (2(2)^{1/2}/(20)^{1/2}a^2) \sum_{N=1}^{\infty} [E_c(N)]_{av} \quad \{103\}CS. \quad (11.2)$$

$$(U_e)_1 = (2(2)^{1/2}/a^2) \sum_{N=1}^{\infty} [E_c(N)]_{av} \quad \{001\}CS. \quad (11.3)$$

The results of the calculations showed that the summations reached a constant level after values of  $N$  equal to or greater than 3, and these values were used in evaluating  $(U_e)_1$ . The final values were found to be

$$[(U_e)_1]_{102} \simeq -8.6 \times 10^{-3} \times \frac{(2 + \delta_{102})}{2} \quad (\text{eV/nm}^2). \quad (12.1)$$

$$[(U_e)_1]_{103} \simeq -6.8 \times 10^{-3} \times \frac{(4 + \delta_{103})}{3} \quad (\text{eV/nm}^2). \quad (12.2)$$

$$[(U_e)_1]_{001} \simeq -2.3 \times 10^{-3} \times (2 + \delta_{001}) \quad (\text{eV/nm}^2). \quad (12.3)$$

The values of  $(U_e)_2$  can be calculated by using the values of  $\sum_i (E_c)_i$  and  $\sum_{i'} (E_c)_{i'}$  obtained above and Eq. (8). The results were calculated as a function of the spacing between the CS planes, for spacings lying in the range 1.1–5.1 nm for {102} CS, 1.1–3.5 nm for {103} CS, and 0.95–5.0 nm for {001} CS. The values found did not vary significantly with spacing, and the steady-state values found were identical to those for  $(U_e)_1$ , viz

$$[(U_e)_2]_{102} \simeq -8.6 \times 10^{-3} \times \frac{(2 + \delta_{102})}{2} \quad (\text{eV/nm}^2). \quad (13.1)$$

$$[(U_e)_2]_{103} \simeq -6.8 \times 10^{-3} \times \frac{(4 + \delta_{103})}{3} \quad (\text{eV/nm}^2). \quad (13.2)$$

$$[(U_e)_2]_{001} \simeq -2.3 \times 10^{-3} \times (2 + \delta_{001}) \quad (\text{eV/nm}^2). \quad (13.3).$$

### 3.2. $(U_e)_{rep}$

As described before, the repulsive coulomb energy between two nonneutral CS values 1 and 2 can be calculated theoretically by

using Eqs. (9) and (10). The first step in this calculation is to obtain the value of  $(E_{rep})_{ii'}$ . In order to estimate the value of  $(U_e)_{rep}$  per unit area of the CS planes, the value of  $(E_{rep})_{ii'}$  must converge to some definite value when we fix  $i$  in the CS plane 1 and change  $i'$  in CS plane 2 or *vice versa*. Unfortunately it was found that for the practical range of  $i'$ , the value of  $(E_{rep})_{ii'}$  did not converge. For example, in the case of two nonneutral {102} CS planes, separated by approximately 0.94 nm, when we have chosen even a block of  $91 \times 61$  units in CS plane 2, the ratio of the minimum value of  $(E_{rep})_{ii'}$  due to a unit on the boundary of the block to the maximum value due to the unit in the center of the block is about (1/50). This means that it is impractical to calculate  $(U_e)_{rep}$  per unit area of CS plane and so we have considered two single crystals of different sizes, one with a height ( $H$ ) of  $\sim 12.1$  nm and width ( $W$ ) of  $\sim 19.9$  nm and the other with dimensions of  $\sim 4.1$  nm  $\times$   $6.9$  nm, where  $H$  and  $W$  are the dimensions shown in Fig. 3(b). We have calculated the values of  $(U_e)_{rep}$  per unit areas in the center of CS plane 1 caused by CS plane 2 or *vice versa* as a function of the spacing between the CS planes  $d_x$ . In Fig. 4 the values of  $(U_e)_{rep}$  for the {102}, {103}, and {001} CS planes are plotted as a function of  $d_x$ , with Fig. 4a corresponding to the larger crystal and 4b to the smaller crystal. The vertical axis in Fig. 4 is  $(U_e)_{rep}/Q$  (eV/nm<sup>2</sup>)/ $Q$  where  $Q = [(2 + \delta_{102})/2]^2$  for {102} CS planes,  $Q = [(4 + \delta_{103})/3]^2$  for {103}, and  $Q = [2 + \delta_{001}]^2$  for {001}; the horizontal axis indicates the spacing between two CS planes,  $d_x$ .

## Discussion

The results described clearly show that the energy terms  $(U_e)_1$  and  $(U_e)_2$  can be neglected in comparison with  $(U_e)_{rep}$  and in all probability these energy terms will not have a profound effect upon the microstructures of crystals containing CS planes. We will therefore not discuss them in detail here. It is clear from the calculations that  $(U_e)_{rep}$  is more likely to be of some importance in this respect, but the present results cannot be interpreted quantitatively because the magnitude

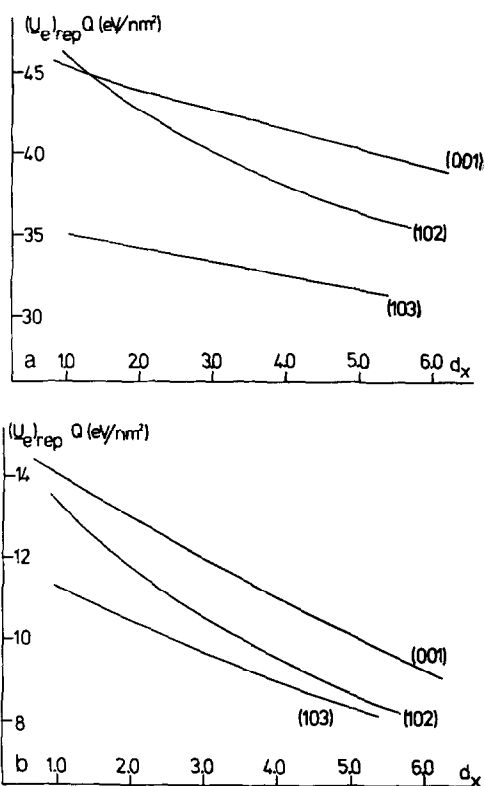


FIG. 4. The repulsive coulomb energy  $(U_e)_{rep}$ , between two CS planes separated by  $d_x$  for (a) a crystal of approximate dimensions  $12.1$  nm  $\times$   $19.9$  nm, (b) a crystal of approximate dimensions  $4.1$  nm  $\times$   $6.9$  nm. The y-axis shows  $(U_e)_{rep}/Q$ , where  $Q = [(2 + \delta_{102})/2]^2$  for {102} CS,  $Q = [(4 + \delta_{103})/3]^2$  for {103} CS, and  $Q = [2 + \delta_{001}]^2$  for {001} CS. The x-axis shows the spacing between the CS planes,  $d_x$ .

of the  $(U_e)_{rep}$  term depends sensitively upon CS plane area and crystal size. Nevertheless, a number of semiquantitative conclusions which are of interest can be drawn from the results and these will be outlined below.

The absolute magnitudes of the  $(U_e)_{rep}$  terms depend critically upon the value of the dielectric constant of the parent oxide, or more precisely upon the magnitude of the dielectric constant in the regions between the CS planes. If the dielectric constant is low, the interaction between CS planes will be high, even at high spacings. This will result in high values for the defect interaction energy in the reduced crystals which may in fact become prohibitively high and make the nucleation

of a new structure or an alternative mode of accommodating oxygen loss energetically preferred. In crystals with open structures, which can potentially support oxygen deficiency by way of *CS* plane formation, a high dielectric constant may thus be a necessity before *CS* plane formation is energetically attractive. It is of interest to note that the two parent oxides best known for the formation of *CS* structures on reduction,  $\text{WO}_3$  and  $\text{TiO}_2$  (rutile), have exceptionally high dielectric constants (8, 9, 11). The same is true of  $\text{H-Nb}_2\text{O}_5$  (12), which is also noted for its ability to form *CS* structures, while  $\text{MoO}_3$ , which does not form extensive series of *CS* compounds, has only a moderate value for its dielectric constant (13) and  $\text{V}_2\text{O}_5$ , with a low dielectric constant (14, 15) does not form *CS* phases on reduction (i.e., in the phase range  $\text{VO}_2$ – $\text{V}_2\text{O}_5$ ). It is therefore possible that a high dielectric constant is a prerequisite for the formation of *CS* structures. The values of the real charges in the *CS* planes; the term  $\delta$  in our equations is, of course, equally important. Indeed, if *CS* planes are electrically neutral then the term  $(U_e)_{\text{rep}}$  will be zero in all cases. The determination of the real charge state within *CS* planes is therefore of particular interest.

The sequence of values for  $(U_e)_{\text{rep}}$  are also of interest. For most of the range of *CS* plane spacings considered the values of  $(U_e)_{\text{rep}}$  are in the sequence  $\{103\} < \{102\} < \{001\}$ . The geometry of these *CS* planes, shown in Fig. 1, reveals that  $\{102\}$  *CS* planes are composed of blocks of four edge-sharing octahedra,  $\{103\}$  *CS* planes contain blocks of six edge-sharing octahedra, while  $\{001\}$  *CS* planes contain infinite strings of edge-shared octahedra. Between  $\{103\}$  and  $\{001\}$  *CS* planes an infinite set exists, consisting of  $\{104\}$  *CS*, with blocks of eight edge-sharing octahedra,  $\{105\}$  *CS*, with blocks of 10 edge-sharing octahedra, and so on. The values of  $(U_e)_{\text{rep}}$  calculated suggested that if they were extended along the series of  $\{104\}$ ,  $\{105\}$ , etc, we would come to a minimum at some *CS* plane type between  $\{103\}$  and  $\{001\}$ . This is a situation similar to that found when the elastic strain energy between two *CS* planes is considered (6), except that in this latter situation the elastic

strain reaches a maximum value. Further calculations to determine the *CS* plane geometry which yields these minima and maxima, respectively, are in progress and will be reported at some future time.

In considering the possible effect of  $(U_e)_{\text{rep}}$  on the microstructures to be found in crystals containing *CS* planes we must rely upon features which will be sensitive to the relative values of  $(U_e)_{\text{rep}}$  only. Despite this restriction, a number of interesting conclusions can be drawn. For example, the results show that the microstructure of very slightly reduced  $\text{WO}_3$ , consisting of  $\{102\}$  *CS* planes, is not a reflection of the electrostatic energy terms calculated here. Figure 4 shows that if electrostatic interactions between nonneutral *CS* planes dominated the formation energy of *CS* planes in slightly reduced  $\text{WO}_3$  then  $\{103\}$  *CS* plane geometry would be preferred to  $\{102\}$ . If, on the other hand, we consider the term  $(U_e)_1$  which is appropriate to an isolated *CS* plane, we see that there is very little to choose between either of the *CS* geometries considered there, and it is unlikely that, should these energy terms be crucial, the  $\{102\}$  *CS* planes would dominate, as they are found to do. Indeed, in terms of the numerical values,  $\{102\}$  *CS* would be the least favorable.

As the spacing between *CS* planes falls, the term  $(U_e)_{\text{rep}}$  would be expected to become relatively more important. For nonneutral *CS* planes, Fig. 4 shows that  $\{103\}$  *CS* planes will generally be preferred, and, except at the smallest spacings,  $\{001\}$  *CS* planes will be the least favorable. For any particular composition  $\text{WO}_x$ , the spacing between the *CS* planes will be in the order  $\{102\} < \{103\} < \{001\}$  which means that an ordered array of  $\{102\}$  *CS* planes will be far less favorable energetically than the equivalent array of  $\{103\}$  *CS* planes. Experimentally it has been shown that reduction of  $\text{WO}_3$  crystals leads to the formation of quasi-ordered arrays of  $\{102\}$  *CS* planes. The present analysis shows that from the point of view of electrostatic energies, and particularly  $(U_e)_{\text{rep}}$ , this situation is less stable than if the reduction was taken up by  $\{103\}$  *CS* planes, and that as the degree of reduction increases, so the difference between the two *CS* plane types becomes more pronounced. It

is clear that the formation energy of {102} *CS* planes must be favorable to cause them to form initially (7) and it is possible that the increase in the electrostatic energy is one of the important factors which contributes to the change of *CS* plane type from {102} to {103} as the degree of reduction increases.

As with the previous discussion, a knowledge of the charge distribution within the *CS* planes is necessary before these speculations can be taken further. However, a certain amount of information on this may be indirectly gained from a consideration of the growth of *CS* planes. In materials containing a high density of {103} *CS* planes, new *CS* planes can be induced to grow under the influence of the electron beam of an electron microscope. It has been found that if the initial set of {103} *CS* planes are fairly widely spaced, for instance about 3.0 nm, corresponding to an oxide  $W_{26}O_{76}$ , the new *CS* planes grow in at a position which minimizes the elastic strain energy of the group (6). This suggests that electrostatic forces such as  $(U_e)_{rep}$  are not dominant at distances of the order of 1.5 nm, and if they were, the new *CS* planes would be expected to lie exactly midway between the existing *CS* planes. If the initial array of *CS* planes is as close as 2.0 nm new *CS* planes do not grow into the array, but instead the crystal vaporizes (10), which may indicate that electrostatic interactions become important at spacings of about 1.0 nm, but other interaction energies, such as elastic strain (6), may also be important in this respect.

In conclusion, we can say that despite the lack of experimental evidence concerning the real charge distribution within *CS* planes in reduced  $WO_3$ , a number of interesting comparisons have emerged between the interaction energy values found for the three *CS* plane geometries considered here. To date, theoretical calculations have also been made on the interaction energy due to elastic strain crystals of reduced  $WO_3$  containing *CS* planes (6) but in these calculations the absolute values of the elastic strain energy were not

obtained. In order to assess the relative importance of these two interaction energies and the extent to which they contribute to the term  $G_i$  in Eq. (4), the absolute values of the elastic strain energies must be calculated and compared with the results presented here. These calculations are now under way and will be presented in the future.

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