JOURNAL OF SOLID STATE CHEMISTRY, 14, 52–65 (1975)

High-Resolution Electron Microscopy of Crystallographic Shear Structures in Tungsten Oxides

SUMIO IIJIMA

Department of Physics, Arizona State University, Tempe, Arizona 85281

Received June 28, 1974

Crystallographic shear (CS) structure in reduced crystals of WO_3 has been imaged at a resolution of 3–4 Å by a high-resolution electron microscope. A large distortion of the WO_6 octahedra sharing their edges at the CS planes has been directly recognized in electron micrographs.

Crystallographic shear occurs preferentially in a particular crystallographic orientation. The preference may be explained by a different degree of distortion along the principal axes in the WO_6 octahedra of the pseudocubic structure of WO_3 crystal.

A model for growth and ordering of the CS planes is discussed.

1. Introduction

Since Magneli (*1*) found a homologous series of transition metal oxides, M_nO_{3n-2}, a number of related structures have been studied. They are based on MoO_3, ReO_3, and TiO_2 type, and their common structural components are MO_6 octahedra. Variations of these compounds, forming a family of structures, can be described in terms of ordered one- or two-dimensional crystallographic shears (CS), the occurrence of which results in systematic elimination of oxygen from the basic structures. Disordered occurrence of the CS planes in the host structures is one of the sources of nonstoichiometry of these compounds.

The simple case of the CS planes occurs in WO_{3-x}. This was first reported as regularly spaced dislocations parallel to $[100]_R$ ($R =$ idealized ReO_3-type lattice of WO_3) by Spyridelis, Delavignette, and Amelinckx (*2*). Later Tilley (*3*) found irregularly spaced CS planes lying parallel to $[120]_R$ in WO_{3-x} with $x = 0.02$, similar to those found in an ordered phase of $W_{20}O_{58}$, in which the CS planes were oriented regularly, parallel to $[130]_R$ (*1*).

Recently, a number of observations have centred on elucidation of the mechanism for the formation of the CS planes and the origin of their ordering. The role of the CS planes is essential to the transformation of those oxides by oxidation or reduction. Four models for the creation of the CS planes, to be described later, have been proposed but none of these satisfactorily explains the experimental evidence obtained up to now.

By using highly controlled electron microscopy, the present author has established a technique for imaging individual MO_6 octahedra in various "block structures", such as $Ti_2Nb_{10}O_{29}$ (*4*) and H–Nb_2O_5 (*5*), and in tetragonal tungsten bronze-type structures, such as $4Nb_2O_5$–$9WO_3$ and $2Nb_2O_5$–$7WO_3$ (*6, 7*). In some cases even point defects with diameters of several angstroms, occurring within a "block" of corner-sharing octahedra of Nb oxides, have been also detected with this method (*8, 9*). During the study of the disordered structures of a Nb_2O_5–WO_3 system with high-resolution electron microscopy, a region of pure ReO_3-type structure has been imaged as a square array of dark dots with a spacing of 3.8 Å, and sometimes it contained the CS planes (*7*). This observation showed that we are able to image directly the structure of the CS planes in WO_{3-x} at atomic level resolution. Such images will allow us to go

Printed in Great Britain

further into detailed discussions on the formation of the CS planes since most information has come from inferences from low-resolution images.

The basis of this method, which has been described elsewhere (*10*), is briefly that the image contrast taken under certain imaging conditions of the microscope will depend on the electrostatic potentials of the crystal projected along the incident electron beam direction, and it can be interpreted in terms of the structure of the crystal.

In the present paper, slightly reduced WO_{3-x} ($x \approx 0.01$) crystals and pure stoichiometric WO_3 crystals have been studied. The emphasis has been on the creation and ordering of the CS planes. The dependence of the formation of the CS planes on crystallographic anisotropy of WO_3 crystals will be discussed.

2. Experimental

The sample of WO_{3-x} was kindly provided by Dr. Allpress of CSIRO of Melbourne and was one of the series of the samples which have been examined previously by relatively low-resolution electron microscopy by Allpress, Tilley, and Sienko (*11*). They were grown by vapor-phase technique and were then reduced by heating under a controlled atmosphere. Pure WO_3 crystals (kindly provided by Professor Sienko) have been also investigated. The detailed procedure for preparing these crystals and their electronic properties has already been reported by Berak and Sienko (*12*).

The samples were ground in an agate mortar, and fine fragments from the samples were collected on holey carbon supporting films. Very thin crystals protruding over these holes were chosen and tilted and rotated to orient one of their principal crystal axes, $[100]_R$, parallel to the incident electron beam. They were examined by a slightly modified JEM-100B electron microscope at 100 kV, as described previously (*5*).

The images were recorded by using eight main reflections in electron diffraction (ED) patterns, i.e., $\{200\}_R$ type, $\{220\}_R$ type, and the 000 beam. Some other reflections, however, also contributed to the images because the crystal structure of WO_3 is pseudocubic. As expected from the ReO_3-type structure, the lattice image has the appearance of two sets of perpendicularly crossed fringes of about 3.8 Å spacings. With modern electron microscopes similar images can be observed without difficulty. They appear over a relatively wide range of focuses (–0.4 to +0.15 μm) of the objective lens (*13*) and have been called "crossed two-beam interference fringes." It is known, however, that in general the image contrast cannot be interpreted in terms of the crystal structure and does not show one-to-one correspondence with atom positions in the crystal. Therefore, to ensure a meaningful discussion of the detailed structure of the CS planes from the recorded images, special attention was paid to maintain the "optimum imaging condition" (underfocusing about 900 Å for our microscope) and to use very thin crystals so that dark regions in the image represent the metal atom positions in the crystal (*10*).

According to the experiment by Allpress *et al.* (*11*) the CS planes can be introduced into crystals of WO_3 by electron beam irradiation, as a result of loss of oxygen. In order to examine the original crystals without radiation damage, every fragment was first subjected to observation of its electron diffraction pattern with a very weak electron beam, and then high-resolution images of the crystals were recorded. When it was necessary to electron irradiate the crystals with strong intensity to induce CS planes, this was done by removing the condenser aperture of the electron microscope.

3. Four Models

Four mechanisms have been proposed for the creation of CS planes. They are briefly summarized below.

a. The "Ordering and Shear" Model of Gado (14)

A large number of anion vacancies produced by loosing oxygen from the crystal surface might migrate into the crystal and order into walls, across which the crystal subsequently shears, annihilating the vacancies. The initial stage of the segregation of the anion vacancies might be seen in an electron diffraction pattern as superstructure spots, but no evidence for this has been found.

b. The "Cooperative Migration" Model of Andersson and Wadsley (15)

Adjacent cation–anion planes parallel to $[100]_R$ move cooperatively into the crystal. The cations jump into adjacent interstices of the ReO_3 structure, releasing oxygen at the surface. By repeating this, the CS planes grow inward from the surface. This model favors an ordering of the CS planes but a large number of both cations and anions must migrate to produce a CS plane, which seems to be improbable. In this model longitudinal movements of the CS planes within their own planes could not be explained.

c. The "Dislocation" Model of Anderson and Hyde (16)

The primary process is the production of random anion vacancies similar to those of Model a, but they first segregate into relatively small planar disks at very low concentration, across which collapse and shear occurs, forming dislocation loops. They act as sinks for further vacancies and can grow to become the CS planes. The experiment by Allpress et al. (*11*) supported this model, but they could not find any of the dislocation loops required for this model. This model does not explain how the CS planes order and move laterally.

d. The "Hairpin" Model of Van Landuyt and Amelinckx (17)

This is somewhat similar to Model b. The creation of the CS planes occurs in a pair at the surface and cooperative migration of both cations and anions takes place, but the active area is only the tip of the "hairpin" which can move into the crystal, leaving a pair of CS planes. This model is based on the observation of a nonstoichiometric rutile. If this is to be considered general, it is necessary to confirm the presence of such "hairpin" structures in other materials.

4. Results and Interpretation

Several polymorphs of WO_3 were reported by Roth and Waring (*18*). Under the condition for taking ED patterns with a very weak electron beam in the present experiment the specimen temperature should be near room temperature, so that the room-temperature monoclinic form of WO_3 will be expected. This is stable at 17–310°C and the unit cell is $a = 7.297$, $b = 7.539$, $c = 7.688$ Å and $\beta = 90.91°$ according to Loopstra and Boldrini (*19*).

Among 30 fragments from WO_{3-x} and 15 fragments from stoichiometric WO_3 examined here, two types of the ED patterns were frequently encountered. Their orientations were determined by comparing the ED patterns with the X-ray data given by Tanisaki (*20*). The two types of the ED patterns were (001) and (010) reciprocal sections of the room-temperature monoclinic form. These patterns were changed in quite different ways during the electron beam irradiation. A similar result has also been confirmed in stoichiometric WO_3 crystals. Thus, instead of regarding the structure of WO_3 as an ideal ReO_3 structure, we shall distinguish the (001) plane from the (010) and describe separately the observations in those planes.

a. Observation in (001) Planes

A pair of ED patterns from the crystal of WO_{3-x} oriented with [001] parallel to the incident beam are represented in Figs. 1a and 1b. They were taken successively with different exposures to electron irradiation. In the initial stage of the electron irradiation (Fig. 1a) streaks are seen along [210] but a few fragments showed the streaks along both [210] and $[2\bar{1}0]$. The intensities of the spots are in good agreement with the X-ray data except for those for (h00) with h odd, which are forbidden reflections in the space group $P2_1/a$ of the room-temperature form of WO_3. Their presence can be explained by multiple reflections. With increasing exposure time, streaks appear along [100] as well as [210], where weak satellite peaks develop, corresponding to a spacing of about 25 Å in the real space (Fig. 1b). The similar development of the streaks along [100] has been also observed in fragments of stoichiometric WO_3 crystal.

Figure 2 shows an image of the a–b section

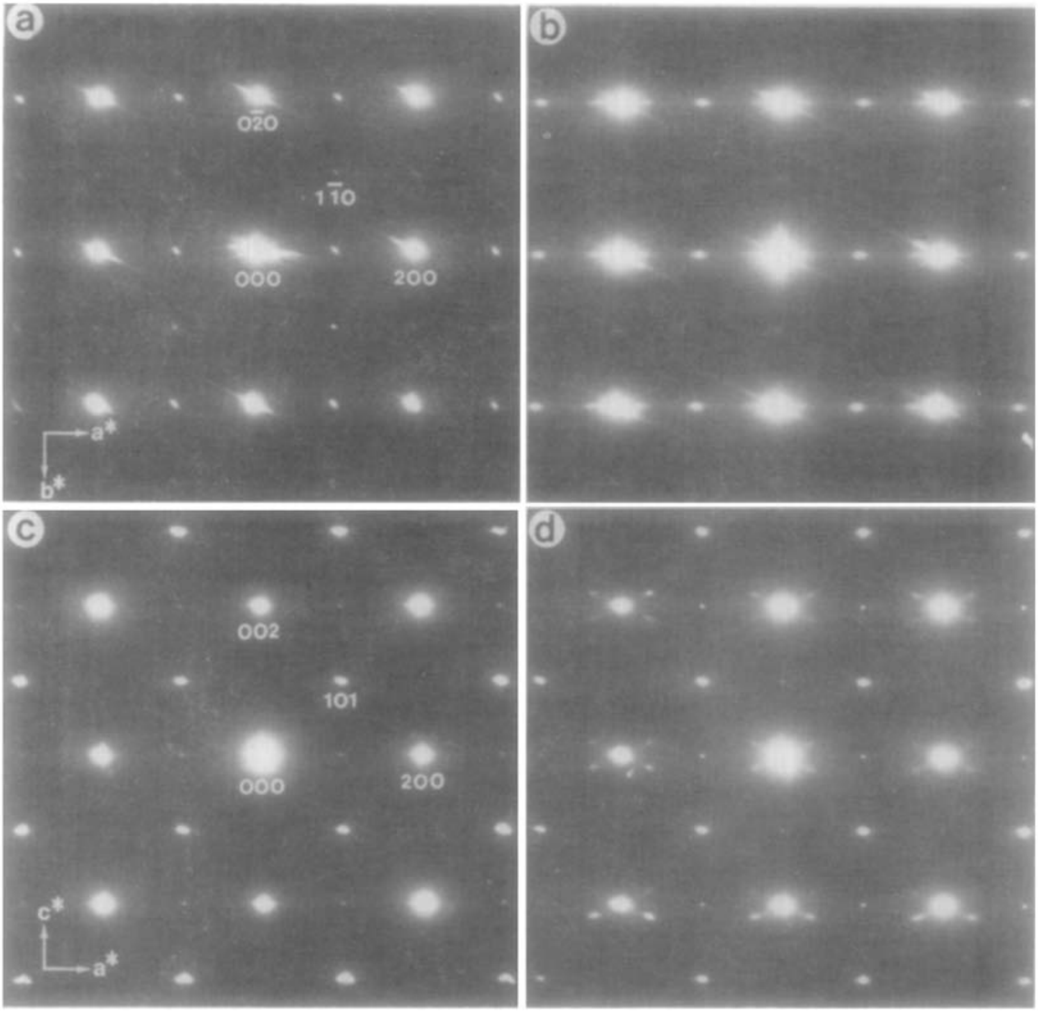

FIG. 1. Electron diffraction patterns taken from slightly reduced WO_3 crystals. (a) The (001) reciprocal section showing streaks along [012], due to presence of the CS planes; (b) from the same crystal as in (a) but after electron beam irradiation, where streaks appeared along [100] with diffused satellites. (c) A (010) reciprocal section where no streaks were observed; (d) from the same crystal as in (d) but after electron beam irradiation, showing development of satellites along both [201] and [20$\bar{1}$], suggesting a superstructure with 20 A spacings.

of the crystal taken in the early stage of the electron beam irradiation. This picture was taken from a very thin crystal under "the optimum imaging condition," so that the black dots forming a square array can be directly compared with the tungsten atom positions in the projection of the structure along [001]. As expected from the streaks in the ED patterns, the CS planes grow parallel to (210). Needless to say, stoichiometric WO_3 crystals did not contain such CS planes at all. As reported by Allpress et al. (*11*), $(210)_R$-type CS planes are thought to have already been present in the original reduced crystals. If the crystal had an ideal ReO_3 structure, the (120) or (1$\bar{2}$0) CS planes that are equivalent to the (210) or (2$\bar{1}$0) in cubic structure would have been present, but they were never observed. Such preferential formation of the CS planes therefore may result from a different degree of distortion in the WO_6 octahedra in the structure of WO_3 crystal.

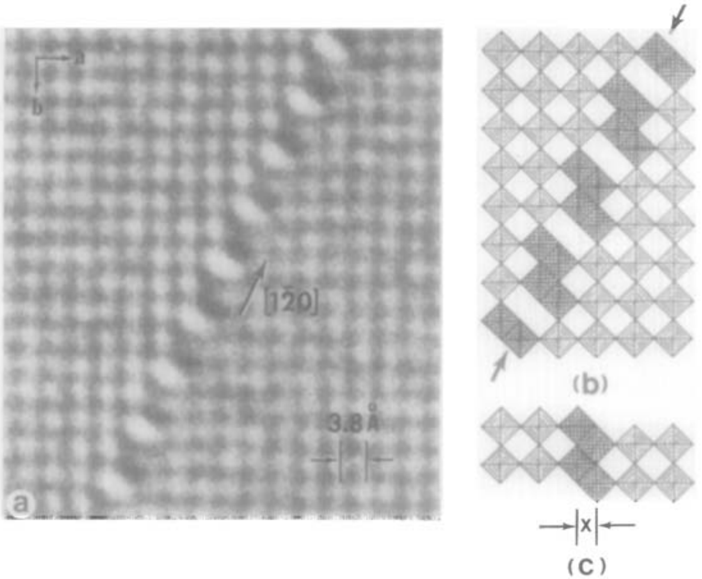

FIG. 2. (a) High-resolution electron micrograph of WO_{3-x} crystal obtained with the electron beam incident parallel to the *c* axis. A prominent feature of the contrast shows the (210) CS plane across which square arrays of the dark dots (indicating W atom positions) are shifted. The contrast distributions are in good accordance with the idealized model of the (210) CS plane (b). However, the image showed that edge-sharing octahedra (shaded) are considerably distorted, so that the distance *X* in (c) is much larger than that in the ideal model.

An idealized model for the (210) CS plane is illustrated in Fig. 2b. The correspondence of the image with the model is apparent where doubled tunnels are imaged as large white dots elongated along [110]. The dark regions along the CS line in the image correspond to the positions where four octahedra share their edges. However, the photograph shows that (100) planes of tungsten atoms with 3.8 Å spacing are displaced across the CS plane by about 2.6 Å, compared with 1.9 Å for an ideal CS plane indicated by the *X* in Fig. 2c. In other words, the octahedra sharing their edges in the CS plane are considerably distorted, and the cations in the octahedra are pushed away from their ideal positions. This is not surprising because electrostatic repulsive energies between cations in the octahedra which share their edges can be minimized by cation displacements away from each other. Such a distortion of the octahedra has been derived by Andersson (*21*) and Allpress (*22*) from their X-ray studies, and they found $x = 2.73$ and 3.08 Å, respectively. It is noted here that the displacement of the (010) planes is measured to be close to 1.9 Å, so that the distortion of the octahedra must be very small along [010].

The correspondence between the image and the structure does not hold for thicker regions of the crystal or in images taken under improper imaging conditions because of nonlinearity between the image contrast and the structure. The figures which follow were not always taken under ideal conditions.

The generation of the (210) CS planes occurred at relatively thicker regions of the crystals with electron beam irradiation. A pair of pictures from the same region of the crystal is shown in Figs. 3a and 3b. White dotted lines in the images show (210) CS planes. The features of the image contrast of the CS planes vary from place to place for the reason mentioned above. There is no doubt, however, that each white spot corresponds to doubled tunnels described in Fig. 2a. At some regions (circled) the CS planes shift slightly in their orientations. A close examination shows that in those regions the CS planes are locally oriented parallel to [130] (note the

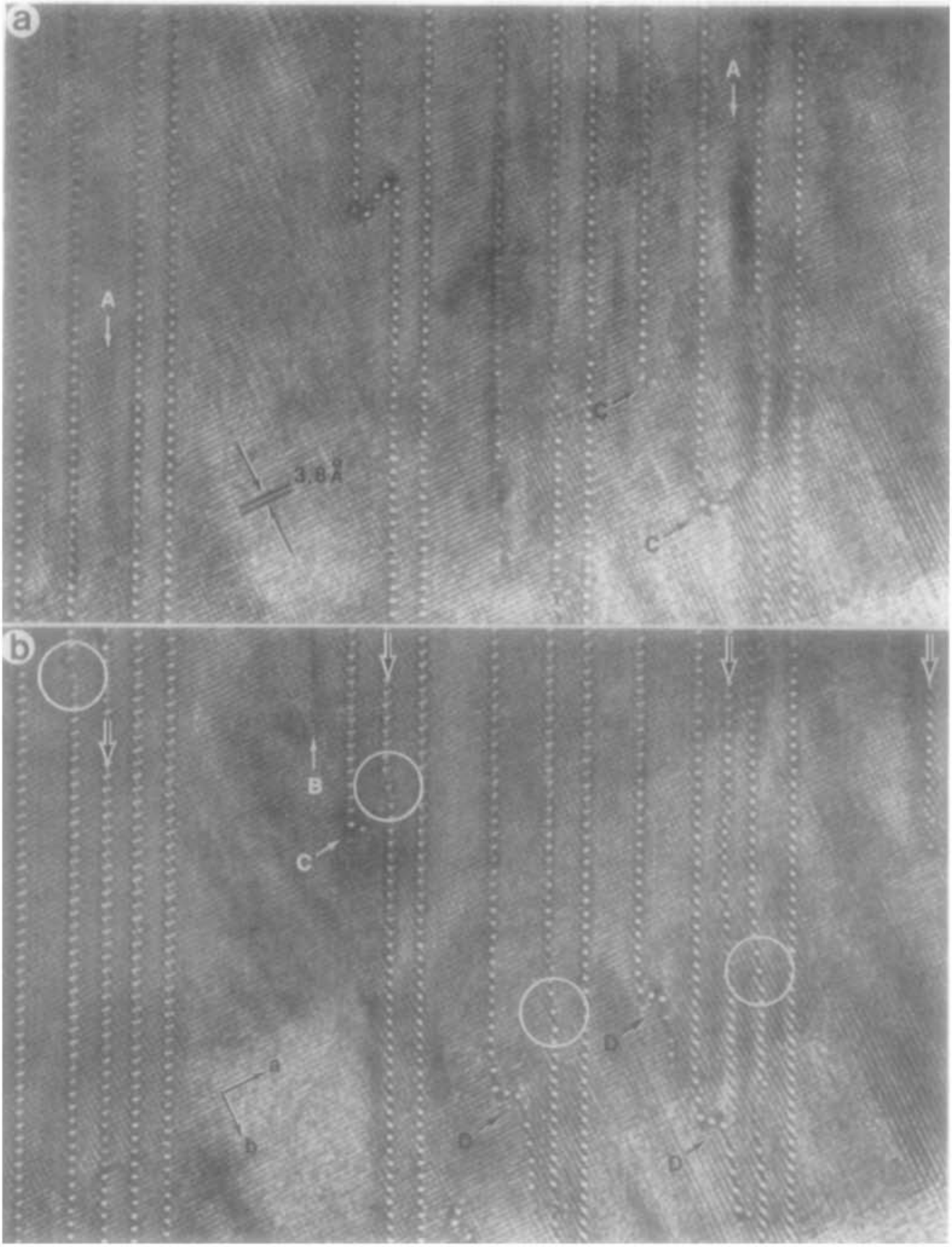

FIG. 3. A pair of electron micrographs of the *a–b* section of WO_{3-x} crystal, showing the effect of electron beam irradiation. White dotted lines show the (210) CS planes. In the beginning of electron beam irradiation (a) dark line contrasts (marked A) appear and become the CS planes with further irradiation (b). Newly formed CS planes are indicated by arrows in (b). Two different types of the termination of the CS planes are marked by B and C. Note "swinging" of the CS planes in the regions enclosed by circles.

distance between adjacent white dots and their orientation). This type of changing of the orientation has been predicted as "swinging shear planes" by Bursill (*23*) and also Allpress (*22*).

In advance of the creation of the CS planes, weak diffuse dark lines appear in some limited areas (marked A in Fig. 3a). Once the CS planes are formed, such contrasts disappear. This reaction occurred almost instantly under intense electron beam irradiation. The newly formed CS planes are indicated by arrows in Fig. 3b. The dark line contrast is probably caused by a strain field in the host lattice, so that disappearance of the dark region suggests that the strain field has been relaxed after the crystal has been sheared. It appears, therefore, that the dark contrast may result from segregation of oxygen vacancies into a planar disk inside the crystal, and subsequently this collapses. In this way a nucleus of a CS plane will be formed. With further irradiation this can grow longitudinally. This is essentially the Anderson–Hyde model for the growth of the CS plane. The black line (marked B in Fig. 3b) shows the termination of the CS plane in the crystal. Allpress et al. (*11*) have proposed a model for the termination of the CS planes in the crysta in reduced WO_3. Their model has a similar structure to the edge dislocation oriented parallel to a principal axis. They thought that oxygen atoms may migrate to the crystal surface through the dislocation line and then be released from the crystal, introducing oxygen vacancies into the crystal. The oxygen vacancies then condense on the dislocation line, and subsequently the dislocation can climb to grow the CS plane. Figure 3 generally confirms their growth mechanism of the CS planes, but the termination has an indistinct region over hundreds of angstroms. This suggests that oxygen vacancies may segregate into a wider strip near the termination of the CS plane rather than on the dislocation line.

Figure 3 shows another type of termination of the CS planes (marked C), around which no dark contrasts develop. Evidently, this type of

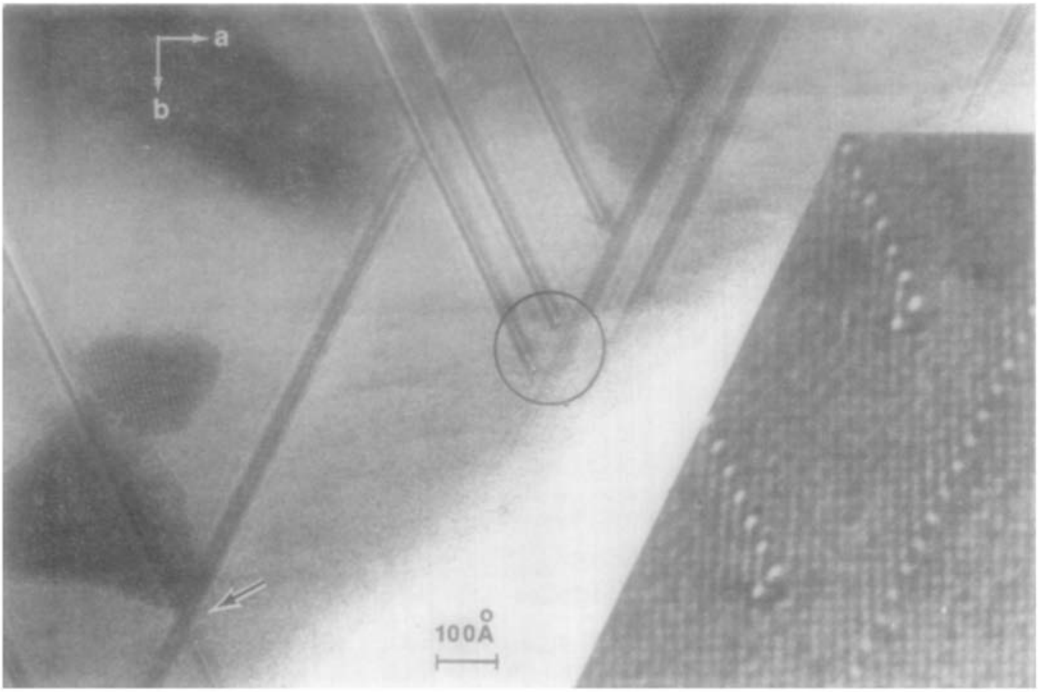

FIG. 4. Intersecting (210) and 2$\bar{1}$0) CS planes. The inset is an enlarged image of the circled region. When the CS planes meet the differently oriented CS planes, they terminate at positions about 25 Å away from the others, but some CS planes seem to grow continuously across the CS plane (arrowed).

termination is not associated with any strain field. With further irradiation CS planes can grow, forming kinks (marked D). Such terminations of the CS planes always occur where the CS planes meet differently oriented ones, as shown in Fig. 4. This figure shows also that the CS planes interpenetrate, but in fact one of those is divided into segments (arrowed). Note that the CS planes are terminated at a position about 25 Å away from the intersecting CS line (Fig. 4, inset). This suggests that some repulsive forces might be acting between the two CS planes.

A particularly interesting finding is seen in Figs. 5a and 5b. The (210) CS plane is accompanied with oscillatory dark and light bands running parallel to the CS plane on both sides (arrowed in Fig. 5a). The periodicity is about 20 Å. With electron beam irradiation, new CS planes were developed near the edge of the crystal with the same periodicity as that of the oscillatory contrast (Fig. 5b). It is likely that the oscillatory contrast results from a strain field occurring around the CS plane; i.e., the cations have been displaced slightly from their original positions in such a way that their displacement vectors do not lie parallel to the [001] direction. There will be two possible origins for the displacement: First, the isolated CS planes are essentially accompanied by a periodic strain field in the host lattice; second, the strain field results from the oxygen vacancies which have been segregated preferentially along the CS planes and periodically in their lateral directions. This will be discussed later.

Figure 6 shows a modulation of spacing of 3.8 Å with a period of about 25 Å. Such an image was observed occasionally in a heavily irradiated specimen. The regions (arrowed) do not show clear lattice fringes along [010], corresponding to the (200) planes. Sometimes

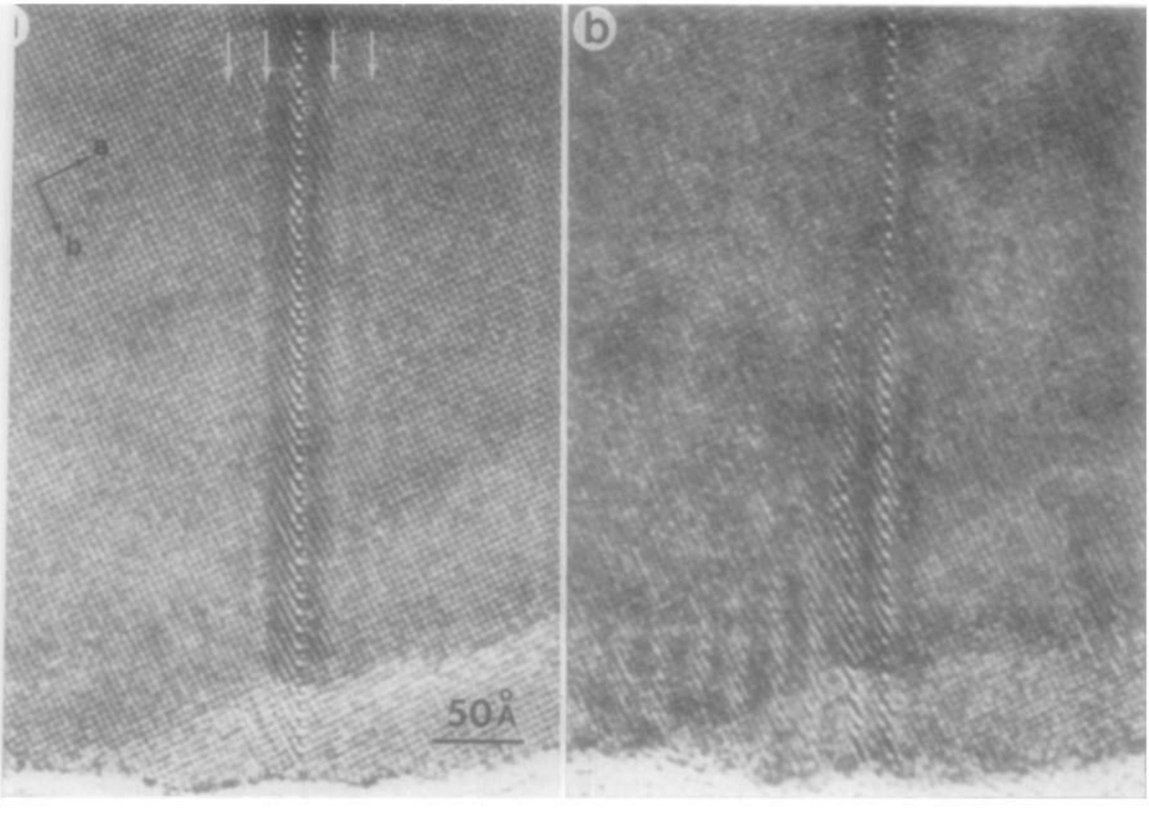

FIG. 5. (a) Oscillatory dark and light contrast bands running parallel to the CS plane on both sides. (b) With electron beam irradiation new CS planes develop with the same periodicity as that of the oscillatory contrast in (a).

the dimension of the whole region of crystal showed a contraction in the [100] direction. This large periodicity is consistent with the observation of the ED pattern (Fig. 1b) with streaks along [100]. As described in the next section, it is attributed to a periodic array of newly developed (201) or (20$\bar{1}$) CS plane which are tilted from the plain on the page.

b. Observations in the (010) Plane

In this plane of the original crystals o WO_{3-x} no CS planes have been found bu

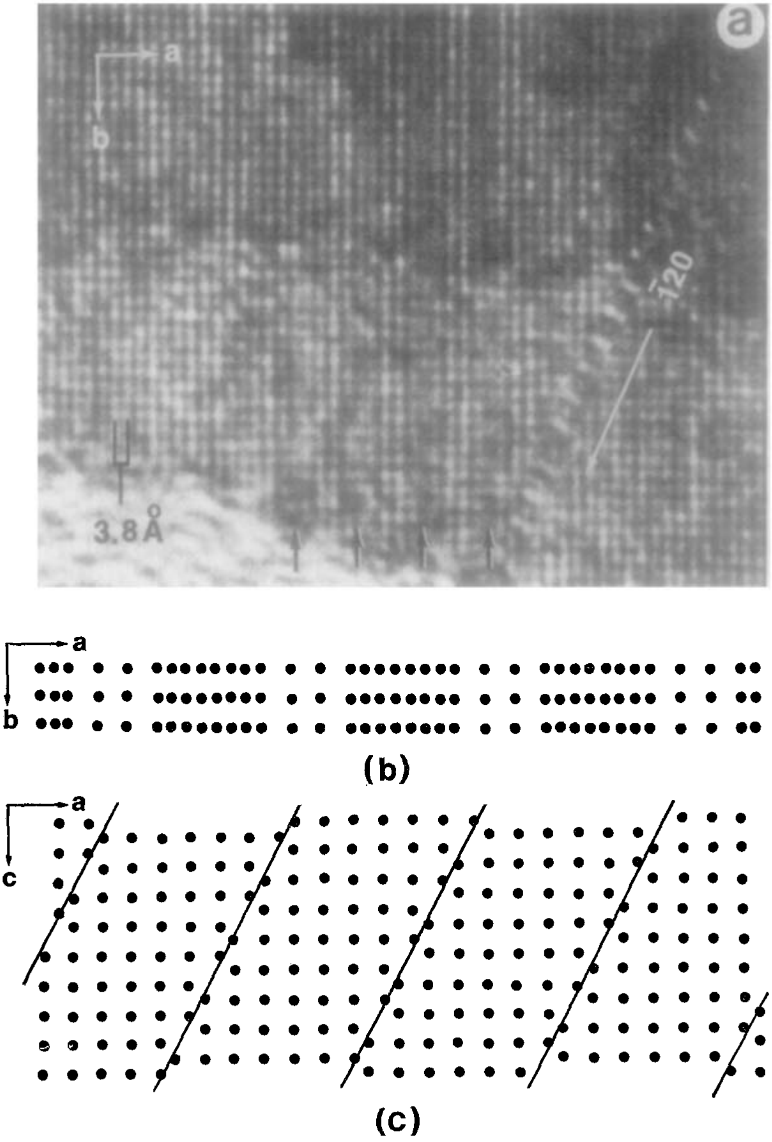

FIG. 6. (a) Modulation of spacing of 3.8 Å with a period of about 25 Å (arrowed), resulting from the periodic occurrence of (210) or (2$\bar{1}$0) CS planes that are not perpendicular to the page. (b) An *a–c* section of the idealized model of regularly spaced (201) CS planes (only cations are shown). (c) The (001) projection of the CS planes in (b). Note that the regions where cations appear closer along the *a*-axis do not show clear lattice fringes in the photograph.

satellite spots developed around the main spots in the ED patterns with electron beam irradiation. Figures 1c and 1d show ED patterns taken with successive increments in exposure time. In Fig. 1c, it is seen that the intensities of the spots of (*h*0*l*)—spots with *l* odd—are much stronger than the (*hk*0) with *k* odd of Fig. 1a. There are also measureable differences in the principal axes. The intensities of the spots were consistent with the X-ray data, so that the crystal is oriented parallel to [010] with respect to the incident electron beam direction.

With further irradiation, satellite spots extend along [201] and [20$\bar{1}$] (Fig. 1d). They correspond to a spacing of about 20 Å in the real space. Similar satellites also developed in crystals of stoichiometric WO_3. If the crystal has the ideal ReO_3 structure, satellites should appear along [102] and [10$\bar{2}$] equivalent to [201] and [20$\bar{1}$], but they were never observed. Such preferential occurrences of the satellites as well as the absence of the CS planes in the (010) planes may be associated again with an anisotropic structure of WO_3 as described in the preceding section. The electron micrographs from a fragment of stoichiometric WO_3 showing these satellites are shown in Fig. 7a. With electron beam irradiation, wrinkle-like patterns develop parallel to [102] and [10$\bar{2}$]. The spacing of the dark bands is about 20 Å. Thus the wrinkles undoubtedly give rise to the satellites in the ED patterns. The image shows, also, that the wrinkles tend to form domains with a parallelogram shape about 100 Å wide and 200 Å long. An enlarged image of a portion of the same crystal is shown in Fig. 7b, but the crystal has been heavily electron irradiated. It was found that two types of CS planes, (201) and (20$\bar{1}$), have developed with an average periodicity of 20 Å (arrowed A) at the regions of black bands of the wrinkles. However, indistinct CS planes (arrowed B) accross which the fringes of (002) planes do not shift are also seen. We suspect that those CS planes have not fully developed

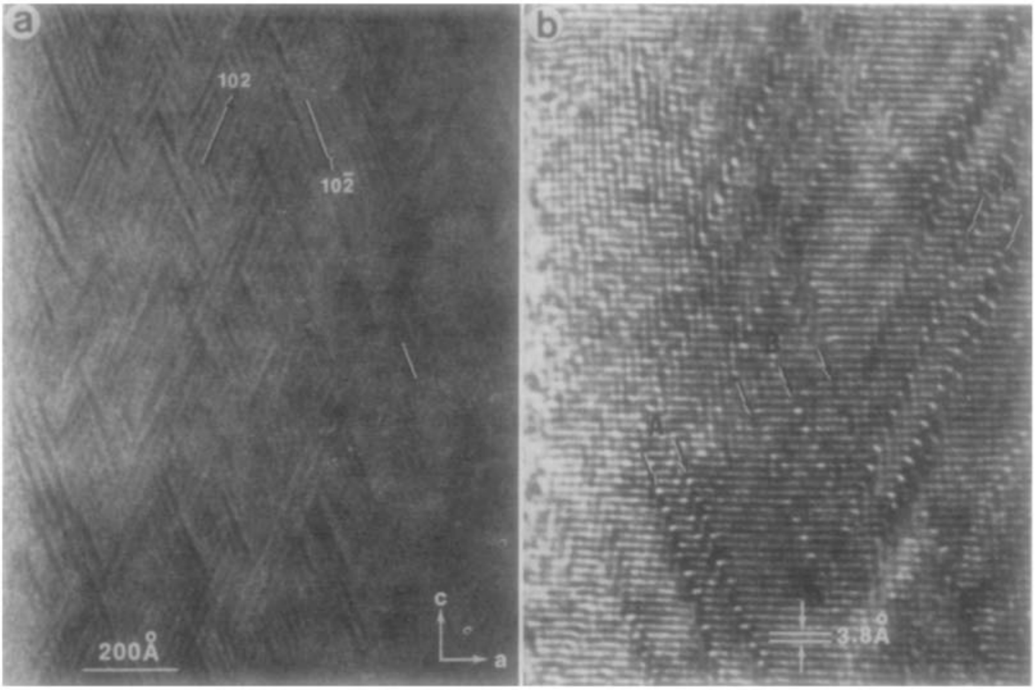

FIG. 7. (a) Wrinkle-like patterns on the (010) plane of stoichiometric WO_3 crystal, induced by the electron beam irradiation. The development of the wrinkles is also clearly seen as superstructure spots in the electron diffraction patterns (see Fig. 2d). (b) With further irradiation some of the wrinkles grew as CS planes.

through the crystal. In other words, those indistinct features of CS planes might be due to oxygen vacancies collapsed into disks, as proposed by Anderson and Hyde (*16*). The disks are bounded by partial dislocations. In most specimens which have been strongly electron irradiated, it was difficult to image a set of the crossed 3.8 Å lattice fringes, probably because of distortion of the crystal. For example, at the upper left-hand corner of Fig. 7b (edge of the crystal) the host lattice of WO_3 is heavily disturbed.

Let us show further evidence that the CS planes could occur only parallel to [010] with electron beam irradiation. Figure 6b shows an idealized model of the regularly spaced (201) CS planes, where only cations are shown. If we look down the *c* axis, the (001) projection of the CS planes may be seen as shown in Fig. 6c. Because of the shear, the array of the cations are displaced apparently by *a*/4 in the projection. If the crystal thickness is reasonably small, sheared regions appear with a large periodicity of about 25 Å along

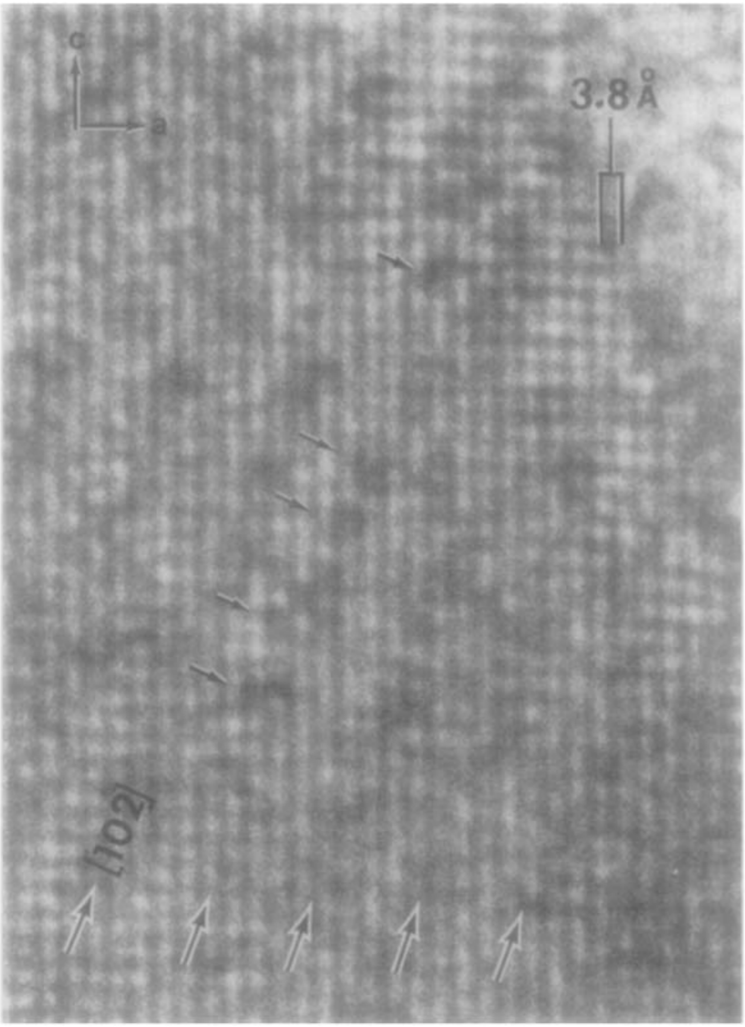

FIG. 8. Initial stage of the wrinkles, indicating that the image contrast of wrinkles (big arrows) are linear arrays of dark blobs (small arrows). These dark blobs may result from some point defects associated with oxygen vacancies.

[010]. The spacing of the arrays of the cations in the superposed regions is about 1.9 Å. This is beyond the resolution of the present microscope, so that only a region showing lattice fringes of 3.8 Å appears periodically. This is what we have seen in the image shown in Fig. 6a. Occurrence of (102) or $(10\bar{2})$ CS planes causes the streaks along [100] in the ED patterns (Fig. 1b) and also contraction of the crystal along [100] as described in Section 4a.

As mentioned previously, the dark contrast in the images may arise from displacements of the cations, so that the wrinkles also may result from strain fields. The periodical appearances of the dark bands indicate that strain fields are formed on regularly spaced slabs in the host structure. It is known that the effect of electron beam irradiation on crystals of WO_3 in vacuum is to produce oxygen vacancies by releasing oxygen atoms from the crystal surface. Thus it is reasonable to consider that oxygen vacancies are segregated into the regularly spaced slabs in the crystal. Evidence for the formation of vacancies was found in a high-magnification image of the individual dark bands in the wrinkles. This is shown in Fig. 8, where the dark bands oriented parallel to [102] are indicated by big arrows. Actually, each dark band is a linear array of dark blobs (arrowed), at which positions lattice fringes with light contrast disappear. This may imply that a tunnel located at the center of the 2 × 2 corner-shared octahedra of the ReO_3 structure (see Fig. 2b) appears occupied by an interstitial cation or else that four cations surrounding the tunnel are displaced from their original positions towards its center. The latter is more probable because interstitials of W ions may not occur in WO_3.

5. Discussion

a. Anistropy in the Formation of the CS Planes

In the present experiment, it was found that in reducing stoichiometric WO_3 crystals at 1022°C, only (210) or $(2\bar{1}0)$ CS planes occurred and no CS planes happened in the (010) planes. Other evidence for the anisotropy is the preferential growth of (201) or $(20\bar{1})$ CS planes by electron beam irradiation. The latter were confirmed in stoichiometric WO_3 crystals.

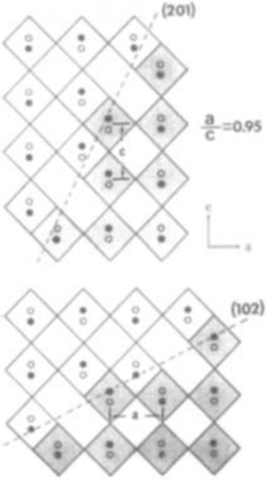

FIG. 9. Two models of the (201) and (102) CS planes. The experiment shows that the edge sharing of the octahedra occurs only along the *a* axis, forming (201) CS planes, because the cation distance is longer along the *c* axis than the *a* axis.

To understand such an anisotropic formation of the CS planes, let us consider why the CS planes always occur on (201) and $(20\bar{1})$ with electron beam irradiation. The structure of WO_3 is not a simple ReO_3 structure but monoclinic due to a slight distortion of the WO_6 octahedra. Figures 9a and 9b illustrate the two models of the (201) and (102) CS planes. Tungsten atoms in a (010) plane are illustrated with exaggerated displacements by solid circles, according to the room-temperature monoclinic form (*19*), and those in the immediately adjacent plane with open circles. The cations make staggered arrays along the *a* axis, but they have an almost cubic arrangement in the (001) plane, so that the *a* axis becomes shorter than the *c* axis. The ratio a/c is 0.95. The difference between these two models may be described in terms of cation distances along *a* and *c*. The experiment shows that the edge sharing of the octahedra occurs along the *c* axis, forming (201) CS planes. As described in Fig. 2, in the actual structure of the CS planes the cations in the octahedra sharing their edges have been pushed away from each other, so that the sharing could be achieved energetically more easily on the (201) plane than that on the (102). This is acceptable because the cation distance is already larger along the *c* axis than the *a* axis.

Similar considerations hold true for the preferential occurrence of the (210) or $(2\bar{1}0)$ CS planes in original reduced crystals rather than the (120) or $(1\bar{2}0)$ because cations are further apart from each other along the *b* axis than the *a* axis; i.e., the ratio a/c is 0.967. For the (100) plane, which we could not distinguish from the (001) in the present experiment, it will not be expected that appreciable CS planes may occur because the distortion of WO_6 octahedra is minimal among the three principal orientations ($b/c = 0.98$). The present discussion is based on the room-temperature monoclinic form of WO_3. An actual structure of WO_3 crystal under the electron beam or the chemical reduction process, however, should have some high-temperature modifications (*18*). Nevertheless, a tendency to have distortion in WO_6 octahedra is still retained even at higher temperatures, so that the preceding discussion will be relevant.

There is a question as to why only the (210) or $(2\bar{1}0)$ CS planes have been formed in the original reduced crystals of WO_3 instead of the (201) or $(20\bar{1})$ CS planes, which were more easily introduced by electron beam irradiation. One possible explanation for this is that, under the conditions of reduction of the pure WO_3 crystals at 1022°C, the crystal structure may be different from the one during electron beam irradiation in the microscope. Although the structure near 1000°C is not known, the largest distortion of the octahedra seems to be along a certain principal axis, and it is only along this direction that the octahedra can shear. Such particular CS planes may correspond to the (210) or $(2\bar{1}0)$ CS planes in the room-temperature form. It appears that there is a preferential orientation of the formation of the CS planes dependent on a reaction temperature.

b. *Ordering of CS Planes*

In the electron beam irradiation experiment, the formation of CS planes was always preceded by dark contrasts. The dark contrasts were thought to be caused by segregation of oxygen vacancies. The formation of wrinkles of 20 Å spacing (Fig. 7) suggested that the oxygen vacancies are ordered in regularly spaced walls in the crystal and subsequently collapse into the CS planes. Accordingly, the origin of such an ordering must be sought in a segregation of the oxygen vacancies.

Now suppose oxygen vacancies are segregated into a particular wall in the crystal; then the surrounding lattice will be distorted. Such a strain field may oscillate laterally around the wall as seen in Fig. 5. Recently, Stoneham and Durham (*24*) studied theoretically the ordering of the CS planes in the ideal ReO_3 structure, and they calculated an interaction energy between a periodic array of CS planes and also between two isolated CS planes by taking into account an elastic strain and a smaller electrostatic contribution. Their particularly interesting result is that the intereaction energy between two isolated CS planes oscillates as a function of the distance between them. We suspect that such an oscillation of the strain field may have been generated along even an isolated CS plane. If this is true, subsequent segregation of oxygen vacancies will occur at regions where the strain energy is minimum. Such regions are periodically arrayed around the initial wall. Thus the walls can propagate laterally by accumulating the vacancies. In this way nucleation of the CS planes arranged regularly may be formed in the host structure. Formation of the wrinkles of Fig. 7a, which appeared in the early stage of electron beam irradiation, supports such an ordering of the oxygen vacancies. Subsequently, the crystal shears to form the CS planes. Incidentally, the *in situ* experiment on the growth of the CS plane that we performed may be far from the condition of chemical reduction of WO_3 crystals and is not in an equilibrium condition. We believe that this causes formation of the domains of the wrinkles or nucleation of the CS planes.

In conclusion, the ordering of the CS planes in WO_3 crystal is partly in accordance with the Gado model, but nucleations of the CS planes do not extend completely through the crystal. The nucleation may be a small CS disk bounded by a partial dislocation loop, and the further growth of the CS planes may occur in a fashion of the Anderson–Hyde model as mentioned in Section 3.

Acknowledgments

The author wishes to thank Professor J. M. Cowley for his continuous encouragement and to acknowledge the support of NSF Grant GH 36667 and of Arizona State University.

References

1. A. Magneli, *Ark. Kemi* **1**, 5 (1950).
2. J. Spyridelis, P. Delavignette, and S. Amelinckx, *Mater. Res. Bull* **2**, 615 (1967).
3. R. J. D. Tilley, *Mater. Res. Bull.* **5**, 813 (1970).
4. S. Iijima, *J. Appl. Phys.* **42**, 5891 (1971).
5. S. Iijima, *Acta Crystallogr. A* **29**, 18 (1973).
6. S. Iijima and J. G. Allpress, *Acta Crystallogr. A* **30**, 22 (1974).
7. S. Iijima and J. G. Allpress, *Acta Crystallogr. A* **30**, 29 (1974).
8. S. Iijima, S. Kimura, and M. Goto, *Acta Crystallogr. A* **29**, 632 (1973).
9. S. Iijima, S. Kimura, and M. Goto, *Acta Crystallogr. A* **30**, 251 (1974).
10. J. M. Cowley and S. Iijima, *Z. Naturforsch. A* **27**, 445 (1972).
11. J. G. Allpress, R. J. D. Tilley, and M. J. Sienko, *J. Solid State Chem.* **3**, 440 (1971).
12. J. M. Berak and M. J. Sienko, *J. Solid State Chem.* **2**, 109 (1970).
13. Keiji Yada and Tadatosi Hibi, *J. Electronmicrosc.* **17**, 97 (1968).
14. P. Gado, *Acta Phys. Hung.* **18**, 111 (1965).
15. S. Anderson and A. D. Wadsley, *Nature (London)* **211**, 581 (1966).
16. J. S. Anderson and B. G. Hyde, *J. Phys. Chem. Solids* **28**, 1393 (1967).
17. J. van Landuyt and S. Amelinckx, *J. Solid State Chem.* **6**, 222 (1973).
18. R. S. Roth and J. L. Waring, *J. Res. Nat. Bur. Stand. A* **70**, 281 (1966).
19. B. O. Loopstra and P. Boldrini, *Acta Crystallogr. B* **25**, 158 (1969).
20. S. Tanisaki, *J. Phys. Soc. Japan* **15**, 573 (1960).
21. S. Andersson, *Acta Chem. Scand.* **18**, 2339 (1964).
22. J. G. Allpress, *J. Solid State Chem.* **4**, 173 (1972).
23. L. A. Bursill, *Nat. Bur. Stand. Spec. Publ.* **364**, 727 (1972).
24. A. M. Stoneham and P. J. Durham, *J. Phys. Chem. Solids* **34**, 2127 (1973).