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On the Generation Mechanism for Shear Planes in Shear Structures*

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A new mechanism is proposed for the generation of shear planes in nonstoichiometric oxides. Previously suggested mechanisms are briefly discussed. Recent observations by transmission electron microscopy on substoichiometric rutile are used to deduce a new model, which is based on the mobility of metal ion interstitials at high temperature.

Introduction

In recent years a number of mechanisms has been proposed for the generation of shear planes in so-called nonstoichiometric oxides such as titanium dioxide and tungsten trioxide. All such mechanisms describe how a "stoichiometric" crystal of the type MO_3 or MO_2 can be transformed into a "nonstoichiometric" one by the regular introduction of "shear planes" generating in this way compounds of homologous series such as M_nO_{3n-1} or M_nO_{2n-1}, also called Magnéli-phases (*1–3*).

The details of the proposed mechanisms are different however; we shall briefly point out the main characteristics of the mechanisms which have been put forward so far. We shall then present some observations which seem to suggest that none of these mechanisms is entirely satisfactory and we shall therefore finally propose a new mechanism which explains the observed geometrical features.

The Different Models

I. "Ordering and Shear" Model

Description

According to this model due to Gado (*4*) the crystal looses oxygen and on doing so anion vacancies are produced which migrate into the crystal and subsequently order into walls across which the crystal subsequently shears, annihilating in this way the vacancies and generating a "shear plane." The model does not give any details about the mechanism by which shear planes can move. The Gado model is pictured in Fig. 1 for the case of ReO_3.

Expected Features

a. Ordering spots should be present in the diffraction pattern *before* the shear structure is formed.

b. Shear planes are always very regularly spaced.

c. No isolated shear planes occur.

Remarks

This very hypothetical model does not agree with the hitherto reported observations.

II. The "Dislocation" Model

Description

In this model proposed by Anderson and Hyde (*5*) the anion vacancies form disc-shaped aggregates which collapse and generate in this way vacancy loops limited by partial dislocations. The dislocations now act as vacancy sinks and attract further vacancies which make the dislocation loops grow by climb extending in this way the shear plane. The mechanism is represented schematically in Fig. 2.

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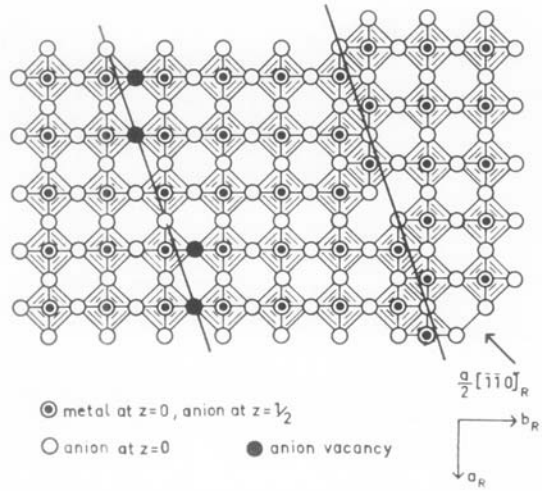

FIG. 1. "Ordering and sheer" model [Gado (*4*)].

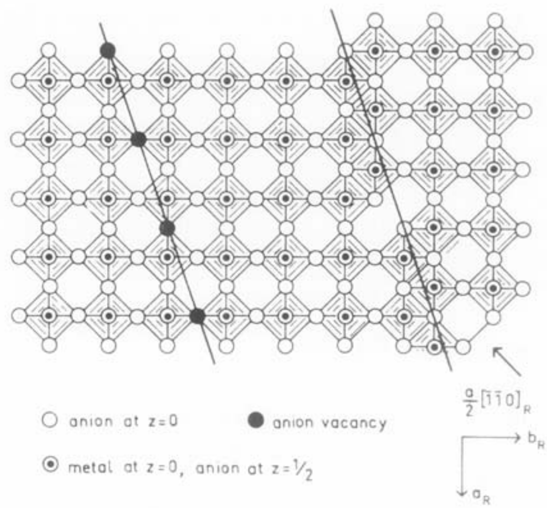

FIG. 2. "Dislocation" model [Anderson and Hyde (*5*)].

Expected Features

a. Initial stages should show faulted loops or shear planes limited by dislocations.

b. Shear planes grow longitudinally.

c. No lateral displacement takes place.

Remarks

Dislocation limited shear planes are only occasionally observed and mostly in materials approaching the stoichiometric composition from larger deviations.

Lateral displacement is necessary for the subsequent ordering of the shear planes into the "shear structure."

III. The "Cooperative Migration" Model

Description

Andersson and Wadsley (*6*) assumed cation planes to move cooperatively into the crystal. The cations jump hereby into adjacent empty interstices in the way shown in Fig. 3. Oxygen is released at the surface each time a cation plane moves into the crystal. The mechanism is represented in Fig. 3.

Expected Features

a. Isolated shear planes are easily accounted for.

b. The crystallography is determined by the surface.

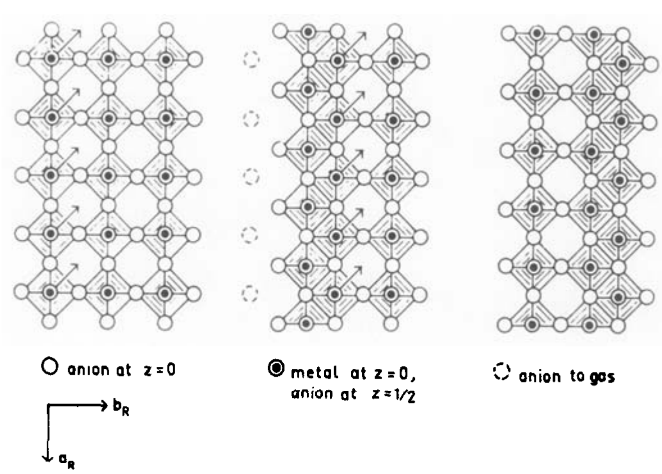

FIG. 3. "Cooperative migration" model [Andersson and Wadsley (*6*)]. Figures 1, 2 and 3 after Bursill and Hyde (*10*).

c. No longitudinal growth of shear planes takes place.

Remarks

As pointed out by Hyde and Bursill (*3*) the occurrence of single shear planes requires the cooperative movement of a very large number of ions. The model does not account for longitudinal growth of the planes. This model implies cation interstitial mobility.

Experimental Evidence

The electron microscopic evidence in relation with the movement of shear planes in titanium dioxide has been summarized in Ref. (*7*). It was shown in particular that:

i. shear planes can move perpendicular to their length direction, implying that a cooperative diffusion movement of titanium is possible within the framework of interstices of the oxygen lattice.
ii. lengthening and shortening of shear planes is occasionally observed suggesting that the shear planes may sometimes be limited by dislocations which can climb.

Whereas (i) suggests mechanism (III), observation (ii) suggests mechanism (II). It should be emphasized that these observations correspond with nearly stoichiometric oxide films in the electron microscope. The observed shear planes are remaining defects after heating of well-ordered shear structures. In an attempt to find evidence which could allow an unambiguous distinction between the different proposed mechanisms, we studied in detail the configuration of shear planes in thin rutile foils prepared

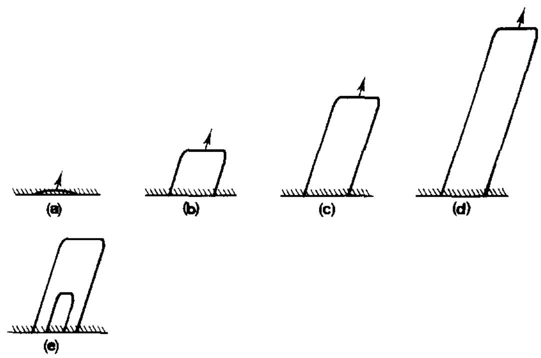

FIG. 4 Schematic illustration of the growth of a "hairpin" (a) through (d). (e) illustrates the aspect of concentric shear planes.

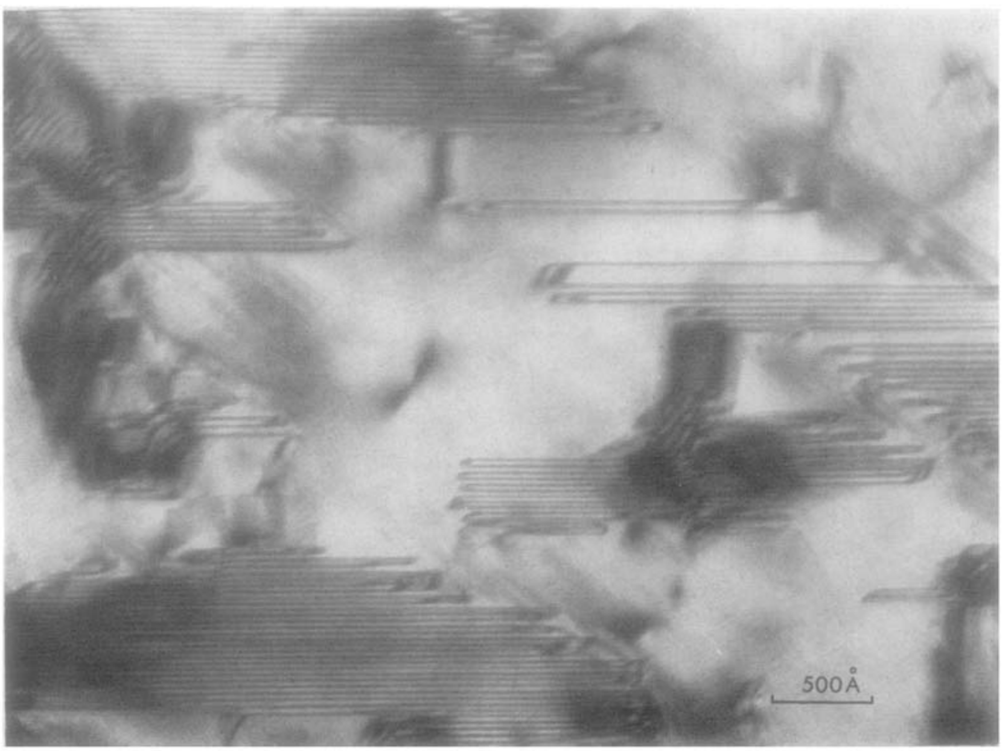

FIG. 5. "Hairpin" shear plane arrangements as observed in nonstoichiometric rutile foils.

by the recrystallization of polycrystalline foils, where special attention was paid to the very initial stages where rearrangement of shear planes takes place.

The most characteristic feature appears to be systematic occurrence of shear planes in pairs, forming "hairpin" shaped arrangements as shown schematically in Fig. 4 and observed in Fig. 5. Concentric hairpins are not uncommon (Fig. 4e). When several parallel hairpins form a finite sequence they adopt configurations such as shown in Fig. 6a and b. Figure 6b clearly suggests a repulsion and consequent movement perpendicular to the length direction. This is also evident from configurations such as in Fig. 7 where the insertion of supplementary hairpins leads to readjustment of the spacing between shear planes. No dislocations are observed at the tips of hairpins.

The New Model

These observations suggest an alternative mechanism for the generation and propagation of shear planes. Although the observations were made on TiO_2 we first illustrate the new mechanism by means of the ReO_3 structure since this makes the representation easier and also because it allows direct comparison with the other mechanisms which were proposed for this structure (Figs. 1, 2, and 3). It is assumed that the "nonstoichiometry" results from loss of oxygen at internal or external surfaces, and the simultaneous inward migration of cation interstitials.

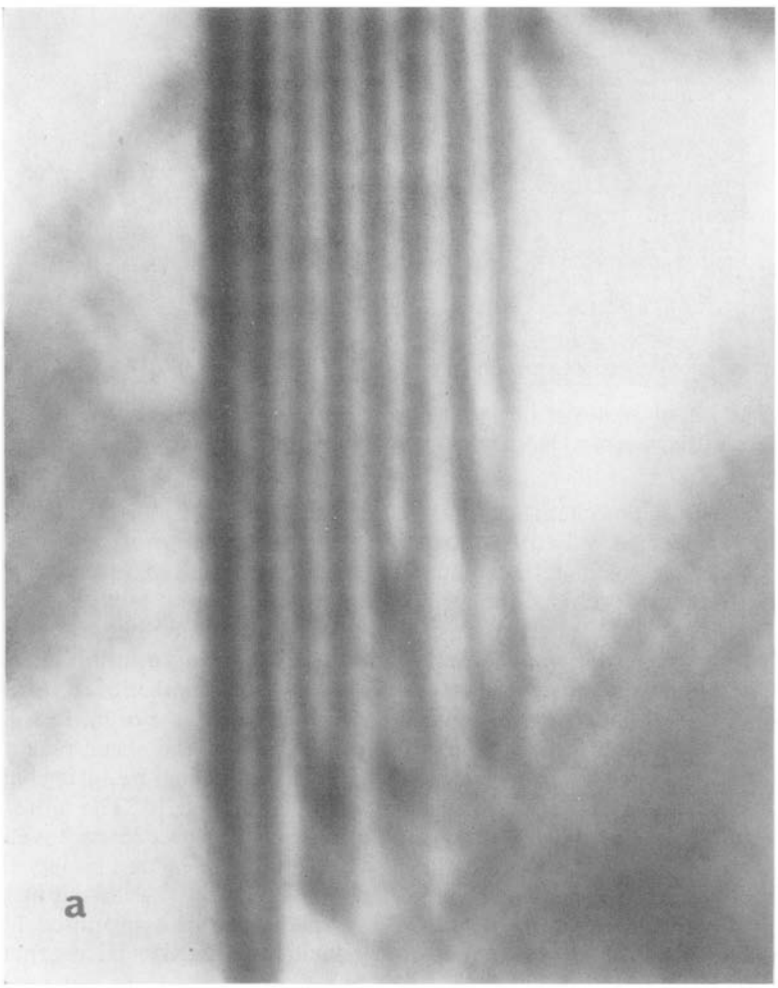

FIG. 6a

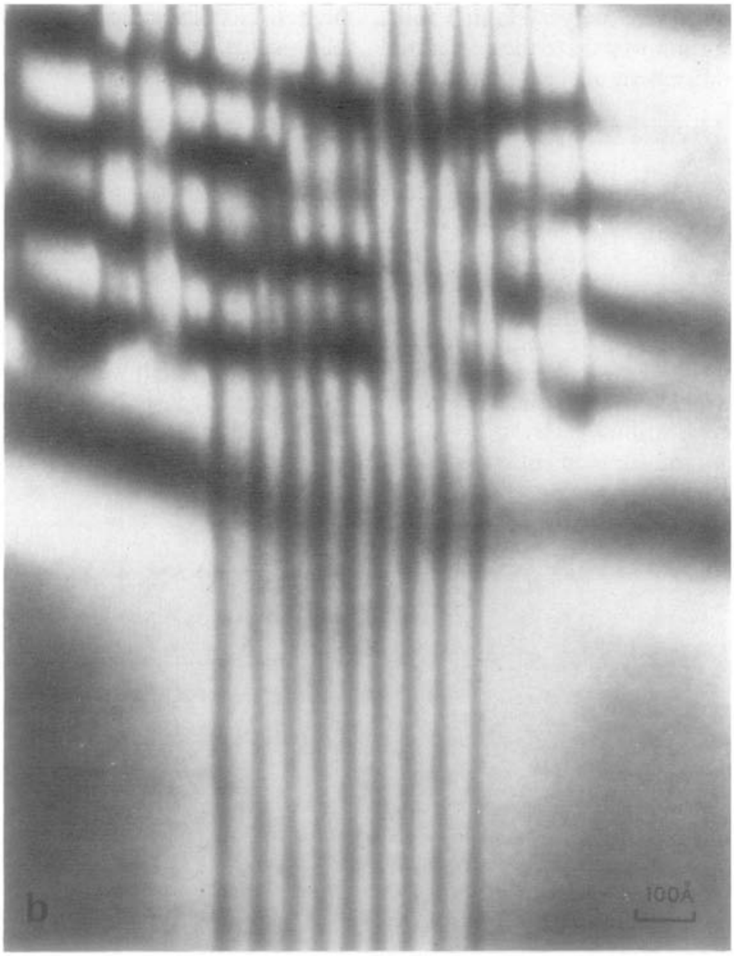

FIG. 6a. Quasi-regular configuration of a limited number of shear planes where the defects are still coupled two by two. (b) Rearranged configuration of a limited number of shear planes.

This is at variance with the mechanisms I and II where the anions are considered to be moving point defects. We further postulate that nucleation of loops of shear planes occurs at the surface in the way shown in Fig. 8, i.e., a narrow strip of anions is lost releasing oxygen and simultaneously a strip of cations moves inwards from the surface. As it appears from Fig. 8, this mechanism depletes one of the (130) faces with respect to the stoichiometric composition, whereas the other face is overfilled. This is due to the fact that the displacement of the ions encloses an angle with the shear plane. Migration of metal interstitials [as indicated by arrows] restores the equilibrium and causes the required composition change at the two faces. The active area is clearly the tip of the hairpin where the cooperative jumps as well as the interstitial migration occurs. The limiting lateral shear planes will move very slowly sideways by the longitudinal propagation of steps (Fig. 9).

The side faces are formed by particularly stable interfaces. The orientation of these faces determines which homologous series is being formed, whereas the concentration of shear planes determines which member of the series is being generated (i.e., the value of n). In some specimens the orientation of the shear planes may change in space as well as in time during anneal. An example is shown in Fig. 10. The more the shear planes deviate from the conservative orientation (i.e., from the planes containing the displacement vector) the more the stoichiometry is changed.

The mechanism proposed here is somewhat related to mechanism III, except that the geometry is quite different. It is not necessary to assume complete sheets to move cooperatively. It is in

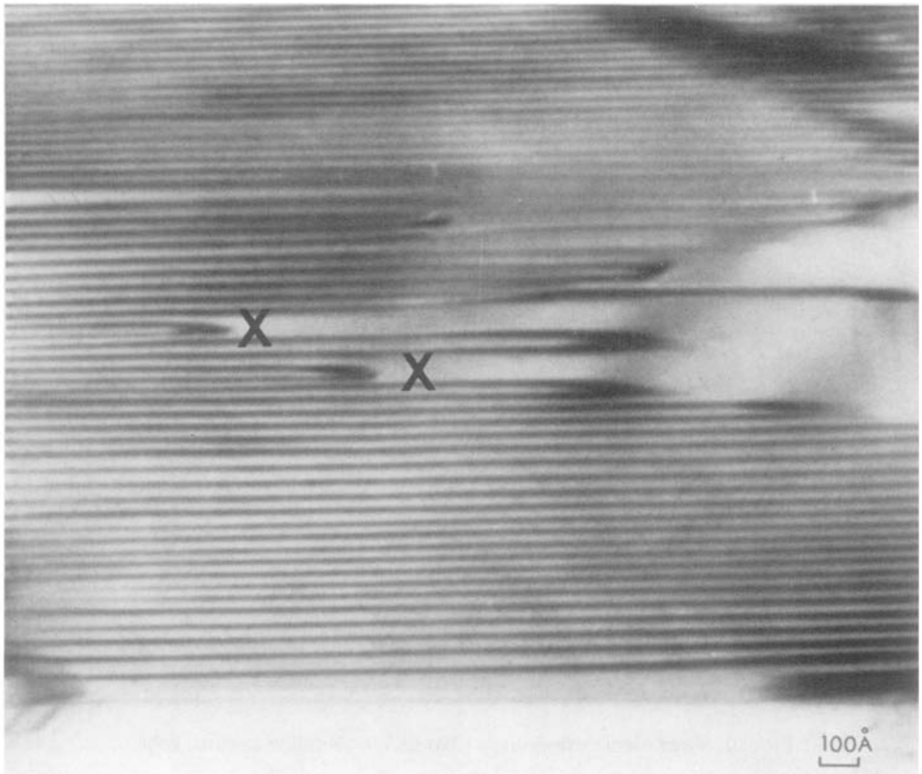

FIG. 7. Irregular sequence of shear planes where isolated hairpins are visible at (X).

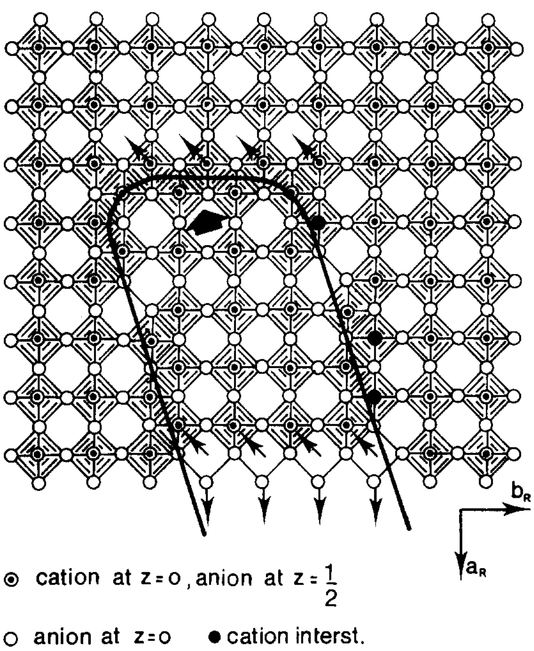

FIG. 8. "Hairpin" model illustrated in the ReO_3 lattice for easy comparison with models I, II and III.

accord with the results of a review paper by Hurlen (*8*) who concludes that the nonstoichiometry in rutile results from titanium interstitials. In a recent critical review Kofstad (*9*) also concludes that at high temperatures and low pressures interstitial titanium ions are the predominating defect in oxygen deficient rutile. The proposed mechanism explains in one model the formation of shear planes, their lateral displacement and longitudinal growth necessary for the

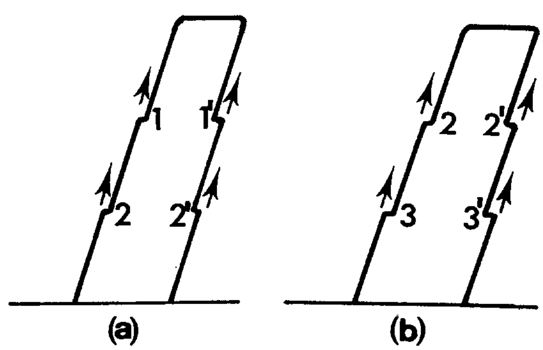

FIG. 9. Schematic illustration of a mechanism for lateral growth by longitudinal propagation of ledges.

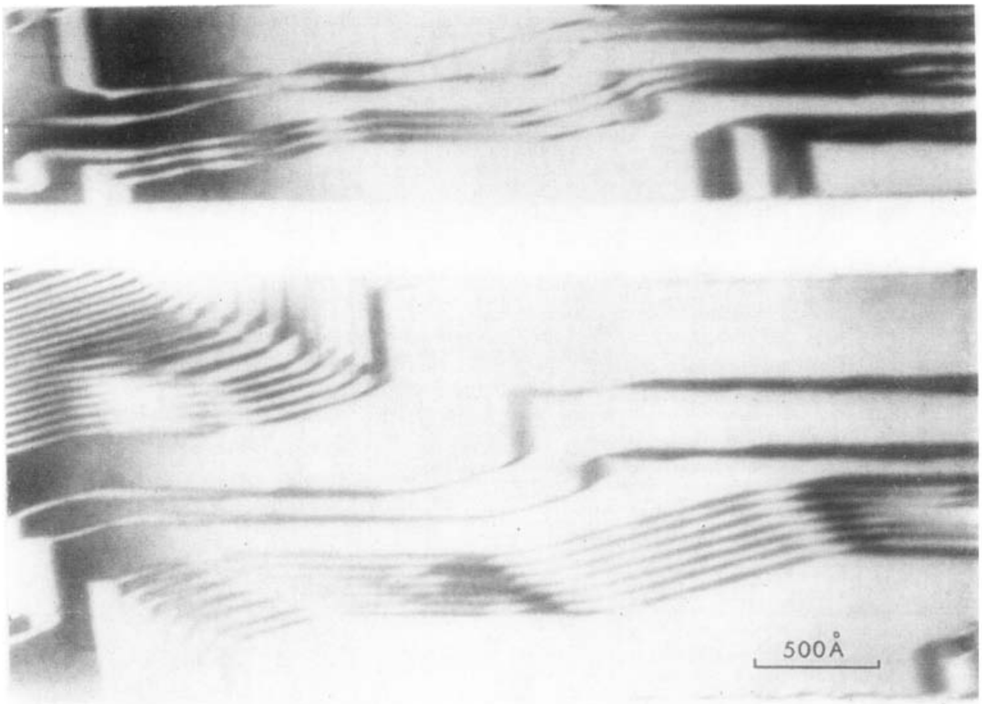

FIG. 10. Shear planes exhibiting a change in orientation in rutile foils.

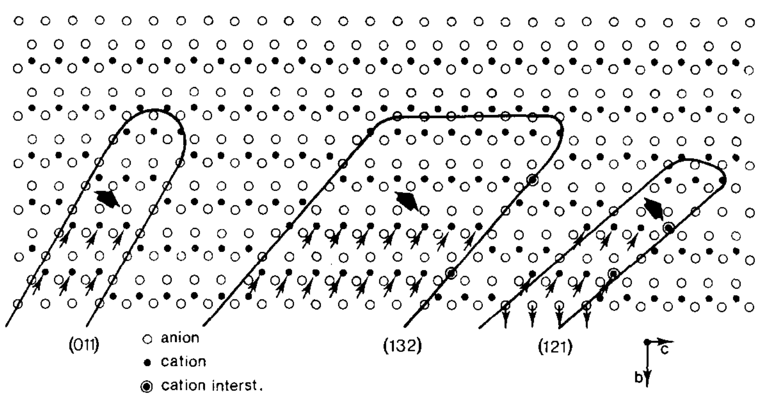

FIG. 11. Hairpin model illustrated for three favorable shear plane orientations in rutile.

formation of shear structures. It is furthermore in agreement with all the hitherto reported observations.

Although our observations were made on thin foils it is suggested that the same mechanism also applies to bulk crystals. Similar hairpin arrangements can be observed on transmission photographs published by Bursill and Hyde on bulk treated rutile (*10*).

A two dimensional representation illustrating this mechanism in TiO_2 for the three most simple types of shear planes {101} {112} and {132} is shown in Fig. 11.

References

1. A. MAGNELI, *Acta Crystallogr.* **6**, 495 (1953).
2. A. D. WADSLEY, in "Non-Stoichiometric Compounds" (L. Mandelcorn, Ed.), p. 98. Academic Press, New York (1964).

3. B. G. Hyde and L. A. Bursill, *in* "The Chemistry of Extended Defects in Non-Metallic Solids," p. 347. North-Holland, Amsterdam (1970).
4. P. Gado, *Acta Phys. Hung.* **18,** 111 (1965).
5. J. S. Anderson and B. G. Hyde, *Bull. Soc. Chim. Fr.* 1215 (1965).
6. S. Andersson and A. D. Wadsley, *Nature (London)* **211,** 581 (1966).
7. S. Amelinckx and J. van Landuyt, *in* "The Chemistry of Extended Defects in Non-Metallic Solids," p. 295. North-Holland, Amsterdam (1970).
8. T. Hurlen, *Acta Chem. Scand.* **13,** 365 (1959).
9. P. Kofstad, *J. Less-Common Metals* **13,** 635 (1967).
10. L. A. Bursill and B. G. Hyde, *Phil. Mag.* **23,** 3 (1971).