JOURNAL OF SOLID STATE CHEMISTRY 22, 135–144 (1977)

Constrained Reactions in Block Structures: Decomposition of $GaNbO_4$

J. L. HUTCHISON AND J. S. ANDERSON

Edward Davies Chemical Laboratories, The University College of Wales, Aberystwyth, SY23 1NE, United Kingdom

Received February 11, 1977; in revised form April 6, 1977

Electron beam induced decomposition of $GaNbO_4$ was followed by high-resolution lattice imaging. The final product was identified as R-Nb_2O_5, implying total depletion of Ga_2O_3 from the system. The transformation took place via a number of new block structures, members of the homologous series $Me_{2n}O_{5n-2}$. A mechanism is postulated, which only involves single stepwise jumps of $\frac{1}{2}a_R\ \langle 110\rangle_R$.

1. Introduction

Many of the ternary oxides of niobium may be classed as "block" structures: two-dimensional crystallographic shear (*CS*) structures in which the ReO_3-type structure is subdivided into rectangular columns or blocks by two sets of intersecting *CS* planes. In a recent electron optical study of the system Ga_2O_3–Nb_2O_5, Gai and Anderson (*1*) found that the stable equilibrium phases were $GaNbO_4$, $GaNb_{11}O_{29}$, and $GaNb_{49}O_{124}$, the latter two phases conforming to well-known block structure types. On the basis of electron diffraction data, $GaNbO_4$ was indexed as a distorted 2 × 2 block structure, isostructural with $AlNbO_4$ (*2*), in agreement with an X-ray structure determination (*3*). A projection of the structure is shown in Fig. 1. In many ternary block structures, the occupation of cation sites appears to be random, but in this structure the site specificity, as between Ga and Nb, is high. Two further compounds, found to have the same structure are $FeNbO_4$, identified by electron microscopy (*4*) and a polymorph of VO_2, prepared by electron beam reduction of V_6O_{13} (*5*).

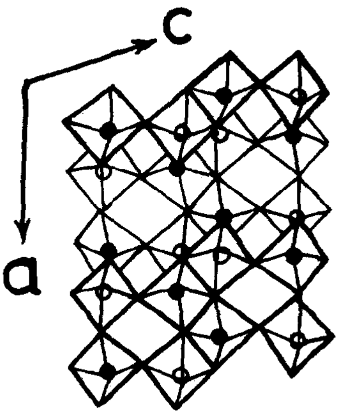

FIG. 1. Structure of $GaNbO_4$, projected onto (010). ○, Ga atoms; ●, Nb atoms.

2. Solid State Reactions and Transformations

Several theories have been advanced to account for the ease with which *CS* planes can be formed or eliminated in reacting crystals (*6–8*). Although the three main theories are quite different in concept, there is good evidence that they are all (in part) correct. The use of high resolution electron microscopy has

ISSN 0022-4596

been to demonstrate the particular systems in (and conditions under) which a particular mechanism may be important. The role of single atom movements, leading to "kinks" in *CS* planes prior to major rearrangements was clearly demonstrated in the oxidation of $Nb_{12}O_{29}$ (*9*), as well as in the in situ reduction of V_6O_{13} (*5*). In addition, the involvement of dislocations in *CS* plane formation has been convincingly shown (*10*). *Linear* propagation of a reaction front, as opposed to the cooperative *planar* process of Andersson and Wadsley (*8*) has been postulated recently by Obayashi and Anderson (*11*) to account for reactions in the WO_3–Nb_2O_5 system.

Carrying out reactions on an electron microscope grid, with the electron beam as the energy source, is not a new procedure. The local conditions of temperature and pressure during reaction are necessarily ill defined, but by careful control of the beam intensity conditions can be established under which reaction proceeds controllably and locally. Using due caution, it is often possible to deduce a probable sequence of events in a reacting crystal, which may undergo solid state transformation, oxidation in the ambient vacuum, or reduction (e.g., by interaction with a carbon film substrate). Thus the beam-induced formation of *CS* planes in the reduction of WO_3 has been followed (*10*) and the initial steps in the oxidation of $Nb_{12}O_{29}$ traced (*12, 13*) in this way.

This paper reports some observations made on the $GaNbO_4$–$GaNb_{11}O_{29}$ system under the influence of electron irradiation and attempts to draw some conclusions regarding the structural changes which occur, in the light of the ideas outlined above.

3. Experimental

The specimen used in this experiment was a biphasic crystal of $GaNbO_4$–$GaNb_{11}O_{29}$ found in a "glassy" oxide of "splat-cooled" $Ga_2O_3 \cdot 3Nb_2O_5$, kindly supplied by Dr. A. M. Anthony (CNRS, Orleans-la-Source). It was during a detailed investigation of the order–disorder phenomena in this material that the experiment was carried out. Use of a biphasic crystal offered the additional advantage that the relative reactivities of the two structures under identical conditions could be assessed directly.

The sample was examined in a Siemens Elmiskop 102 electron microscope using procedures described elsewhere (*11*). The crystal was identified by the *hol* diffraction pattern and lattice images were recorded at a magnification of 500 000×. Reaction was induced in the crystal by defocusing the electron beam, removing the condenser aperture, and carefully refocusing the beam until a visible change was detected in the image. The aperture was then replaced and after readjustment of focus and astigmatism, images were recorded.

4. Observations

Figure 2 is a *hol* lattice image of well-ordered $GaNbO_4$ (A) intergrowing with partly disordered $GaNb_{11}O_{29}$ (B) in which strips of metastable $GaNb_5O_{14}$ are present [(3×3) blocks]. The interface between the two structures is irregular, but there is apparent crystalline continuity. However, the mismatch of dimensions between the $(4 \times 3)_\infty$ and the $(2 \times 2)_\infty$ structures is such that no fully coherent interface is possible between them, and the quasi-coherent intergrowth that is observed necessarily implies that there must be a number of dislocations at the boundary. Planar defects are entirely absent in the $GaNbO_4$ region which does, however, show occasional dark regions (circled in Fig. 3) which strongly suggest "overlap" contrast with an increase in projected charge density.

After intense beam heating dark chevrons appear in the image, as shown in Fig. 4. In these chevrons the dark contrast extends along (200) and $(20\bar{1})$ planes of the host. Their length varies from 6 Å (one-unit cell) to over 50 Å. These features were found in greater numbers as the crystal thickness increased,

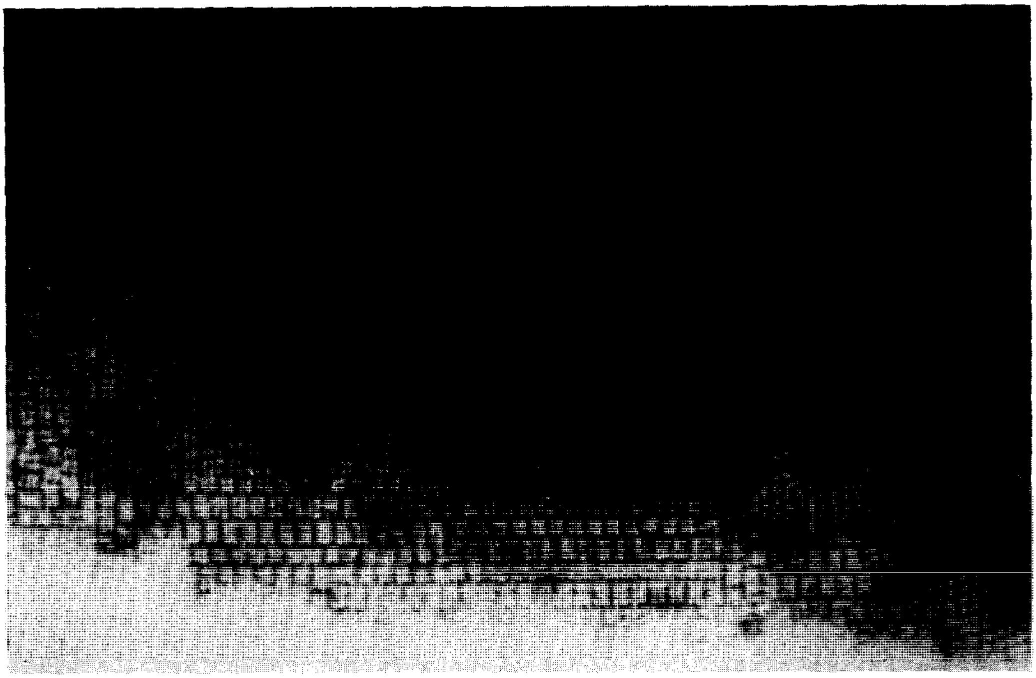

FIG. 2. *hol* lattice image of $GaNbO_4$ (right) intergrown with $GaNb_{11}O_{29}$ (left).

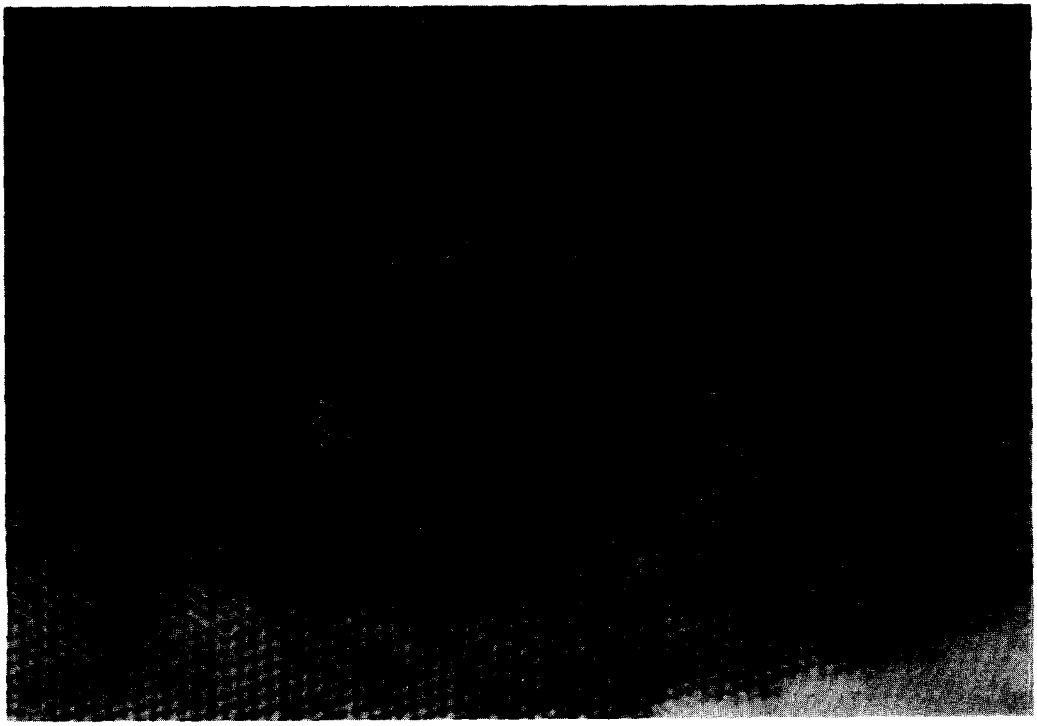

FIG. 3. Enlarged *hol* image of $GaNbO_4$.

FIG. 4. Appearance of dark "chevrons" in $GaNbO_4$ after intense electron irradiation.

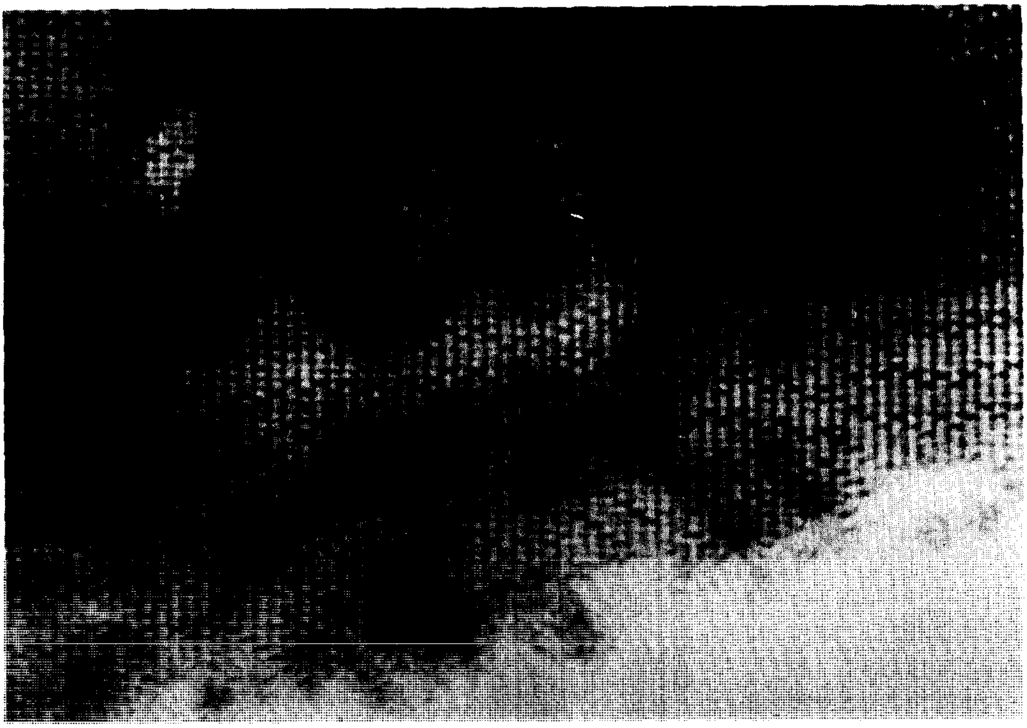

FIG. 5. New structure, a coherent mixture of (4 × 2), (5 × 2), and (6 × 2) blocks, formed after further irradiation.

TABLE I

MEMBERS OF $Me_{2n}O_{5n-2}$ HOMOLOGOUS SERIES

n	O : Me	Ga/Nb oxide	Other oxides
2	2.000	$Ga_2Nb_2O_8$	VO_2, $AlNbO_4$, $FeNbO_4$
3	2.167	$Ga_2Nb_4O_{13}$	V_6O_{13} (*14*)
4	2.250	$Ga_2Nb_6O_{18}$	$Mg_4Nb_4O_{10}F_8$ (*15*)
5	2.300	$Ga_2Nb_8O_{23}$	
6	2.333	$Ga_2Nb_{10}O_{28}$[a]	
"∞"	2.500	—	R-Nb_2O_5 (*16*)

[a] It is interesting to note that the $(3 \times 3)_\infty$ form of $GaNb_5O_{14}$ was found as frequent lamellar intergrowths in $GaNb_{11}O_{29}$ (*1*) and also occurred as such in the present sample. It is a metastable phase in the Ga–Nb–O system but, as will be shown, it is less unstable than the $(2 \times 6)_\infty$ form.

suggesting that they nucleated within the crystal, with little or no surface influence.

Further electron beam heating brought about major structural changes as can be seen in Fig. 5. Here the basic block structure has altered from $(2 \times 2)_\infty$ to a mixture $(2 \times 4)_\infty$, $(2 \times 5)_\infty$, and $(2 \times 6)_\infty$. These new structures correspond to members $n = 4$, 5, and 6 of the homologous series $Me_{2n}O_{5n-2}$. Compositions corresponding to successive members of this series are listed in Table I.

After further irradiation, small areas were observed in which the blocks had assumed great length. These may be regarded as small domains of "$(\infty \times 2)_\infty$" which, as indicated in Table I, is R-Nb_2O_5. Just before the crystal finally decomposed or "melted," substantial areas of this were observed, as in Fig. 6, implying near total depletion of gallium from these localities.

5. Interpretation of Results

Any mechanism which attempts to explain these observations must take the following into account.

(a) The number of interfaces between blocks, in which octahedra share edges, is lowered: *CS* planes are eliminated.

(b) Ga_2O_3 must be removed from the system during reaction, in order to account for

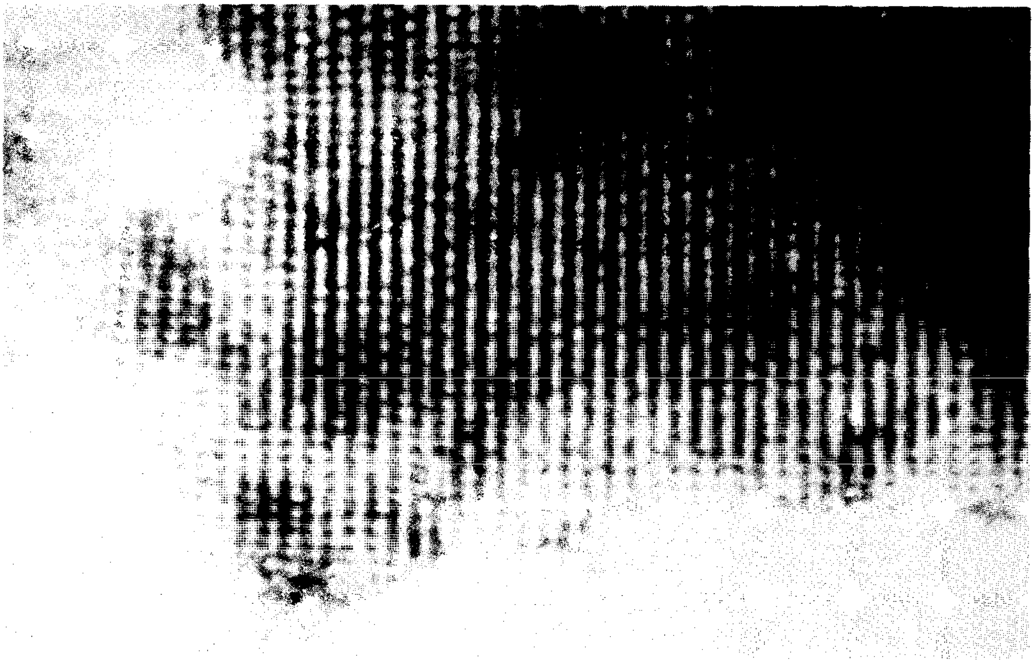

FIG. 6. Lattice image, showing the appearance of R-Nb_2O_5, after prolonged electron irradiation. A "melt front" is seen advancing from the left.

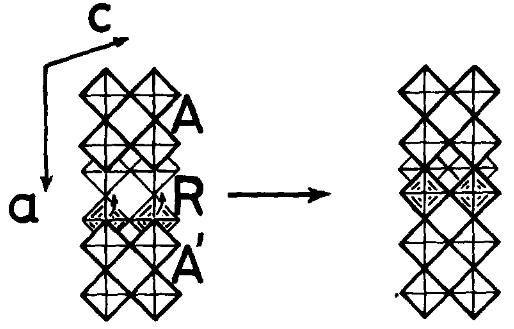

FIG. 7. Proposed atom movements in the initial stage of the beam induced reaction.

the overall composition which is defined, at each stage, by the observed structures (Table I); it can reasonably be assumed that niobium remains in the +5 oxidation state. Since $GaNbO_4$ is a stable phase, coexisting with $GaNb_{11}O_{29}$ over a wide temperature range, it is thermodynamically improbable that Ga_2O_3 is segregated as such (e.g., as an amorphous surface layer). Reduction by the carbon suport, or by traces of hydrocarbon etc., in the vacuum system, could, however, result in the formation and volatilization of Ga_2O from the exceedingly small heated sample.

(c) The transformations appear to originate within the bulk of the crystal and are not restricted to the surface.

(d) The transformations are conservative in *volume*. The product blocks occupy identically the same space as the reactant blocks transformed. There is a loss of *atoms* from the transformed volume, implied by change of composition, which is balanced by the elimination of *sites* as the concentration of *CS* planes is lowered.

We therefore postulate the following possible atom movements, which are consistent with the lattice images and only involve single, stepwise diffusion jumps. The initiating reaction step is shown schematically in Fig. 7. At some point within the crystal, in the block labeled R, a pair of adjacent cations (shaded octahedra) jump by $\frac{1}{2}a_R\langle 110\rangle_R$ from one cation level to the next (i.e., $y = 0$ $y = \frac{1}{2}$). The result is that, at the level $y = \frac{1}{2}$, the two adjacent blocks A and A′ are fused together to form a (5 × 2) layer, identical in area with the three (2 × 2) blocks A, R and A′ involved, but with two interstitial cations left in octahedral positions (at $y = 0$), as relicts of the original (2 × 2) block R. These will give rise to dense overlap contrast, as seen in Figs. 3 and 4, the chevrons indicating where the process has been propagated along a ribbon of blocks, by analogous steps and at the same level occurring in adjacent blocks. We note that similar contrast can be seen in the lattice image of $FeNbO_4$ (*4*), but is not discussed in the text. The initiating step thus creates a single (5 × 2) layer within the three columns A, R, A′, as shown in Figs. 8a and b. By the repetition of the unit jump at successive cation levels, the process can propagate itself along the *b*

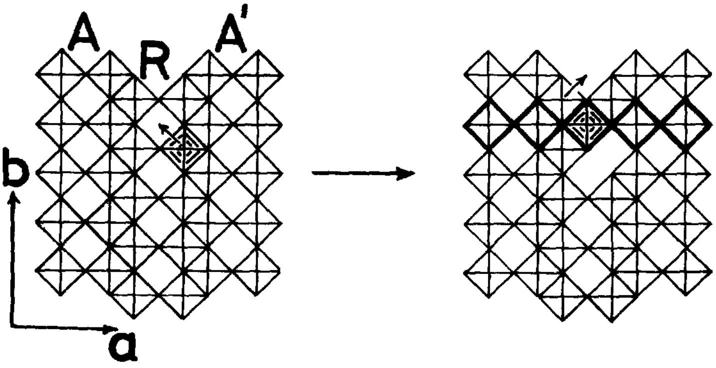

FIG. 8. Creation of a single (5 × 2) block (heavy outline) within the crystal. Unit-step jump is indicated by arrows and is identical for initiation (left) and propagation (right).

direction, thus transforming three columns of (2 × 2) structure to one column of (5 × 2) structure. It has not infrequently been observed, in *CS* structures, that unit displacements are propagated in this way along a unique direction, the zone axis of the family of *CS* planes involved. Since the (5 × 2) product blocks are initiated in single layers, they are not readily detectable in their earliest stages of formation; the only indirect evidence is the overlap contrast arising from the interstitials. For the continuation of reaction, the interstitial cations must migrate out of the lattice (as shown by arrows in Fig. 8); this probably involves diffusion parallel to the *b* direction along the square channels between octahedra, generating complete columns of new structure. Noteworthy but repeatedly observed in defect block structures, is the recovery of one-dimensional order, along the *b* direction.

Jumps occurring in two successive blocks along *a*, in opposite directions, would produce (4 × 2) and (3 × 2). Thus, by means of this initial step it is possible to generate (3 × 2), (4 × 2), and (5 × 2) blocks which then propagate along *b*. (3 × 2) blocks were not encountered however, and it seems likely that on formation they then fused.

The reaction step involves the cooperative movement of a pair of cations and the oxygen atom lying between them. If only one cation executes a jump the resulting configuration is highly strained and a dislocation is introduced. Such features were occasionally observed, as in Fig. 9. In this case, the clarity of the image suggests that the dislocation line lies along the *b* direction, and extends completely through the specimen. The detailed structure deduced for this core is shown in Fig. 10. The structural implications of dislocations in block structures, and the constraints upon them, have been discussed in another place (*15*).

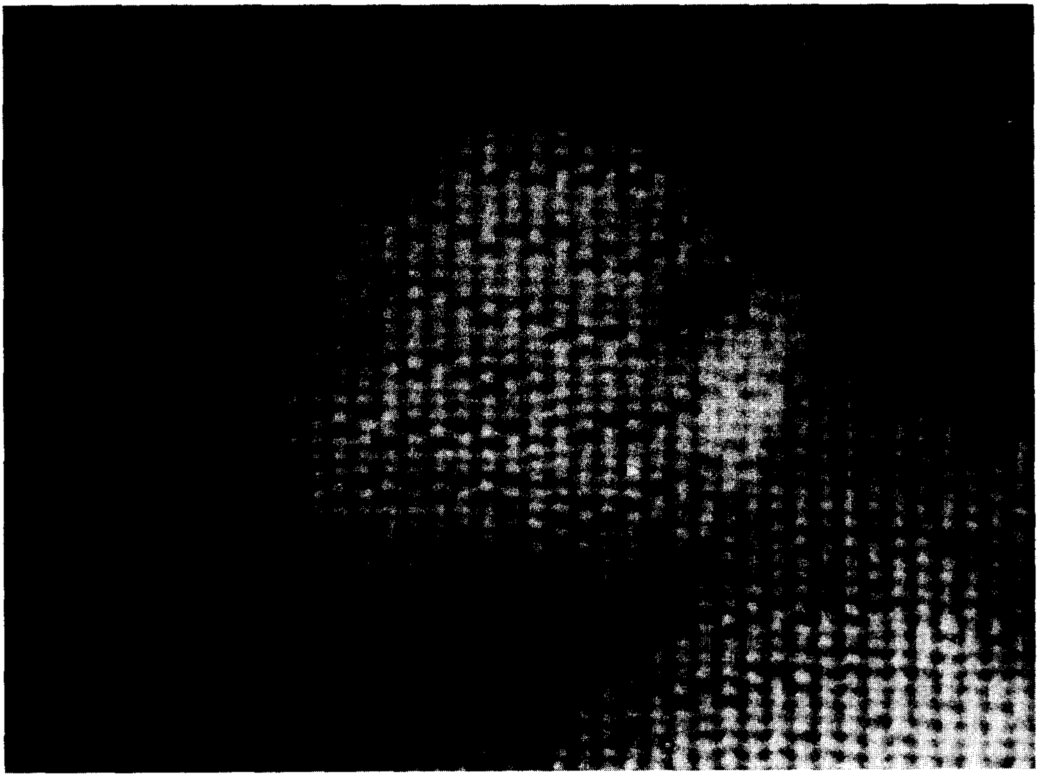

FIG. 9. Dislocation associated with termination of a (stepped) *CS* plane within the crystal.

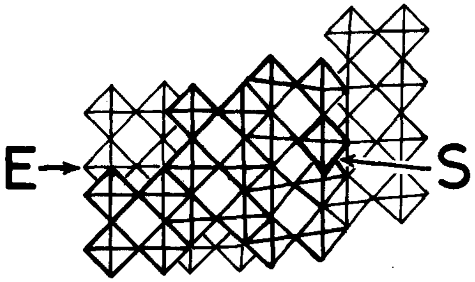

FIG. 10. Idealized structure of core of dislocation in Fig. 9, revealing both edge (elimination of anion/cation row E) and screw (change in octahedron within one block at S) character.

Formation of *R*-Nb_2O_5 upon continued beam heating can now be explained in terms of the repeated fusion of longer blocks to give, as a final product, infinitely long strips, two octahedra wide. This could be accomplished quite smoothly by the same unit step process. Although the $GaNb_{11}O_{29}$ and $GaNb_{49}O_{124}$ structures are the stable structures for a high Nb:Ga ratio, their constituent blocks, three octahedra wide, cannot form an extended coherent boundary, free from faults, with any arrangement of blocks two octahedra wide. Attainment of true equilibrium would therefore involve a drastic reshuffling of *CS* interfaces, and the processes leading to the linear extension of (2 × *n*) blocks are presumably favored kinetically under the conditions of reaction. This reshuffling of *CS* interfaces is not completely inhibited, however, and Fig. 11 shows one isolated block of the $GaNb_{11}O_{29}$ structure in a matrix of (2 × *n*) blocks. The probable structure of the region encircled is shown schematically in Fig. 12. The (4 × 3) block has been formed from two (4 × 2) blocks by one step of Wadsley–Andersson *CS* interface migration laterally, coupled necessarily with some rearrangement of the extension and the linkage of the surrounding (2 × *n*) blocks. By contrast with the region of original $GaNbO_4$ structure, the domain of $GaNb_{11}O_{29}$ underwent no structural changes (i.e., no loss of Ga_2O_3) prior to melting, which advanced across the crystal as a front.

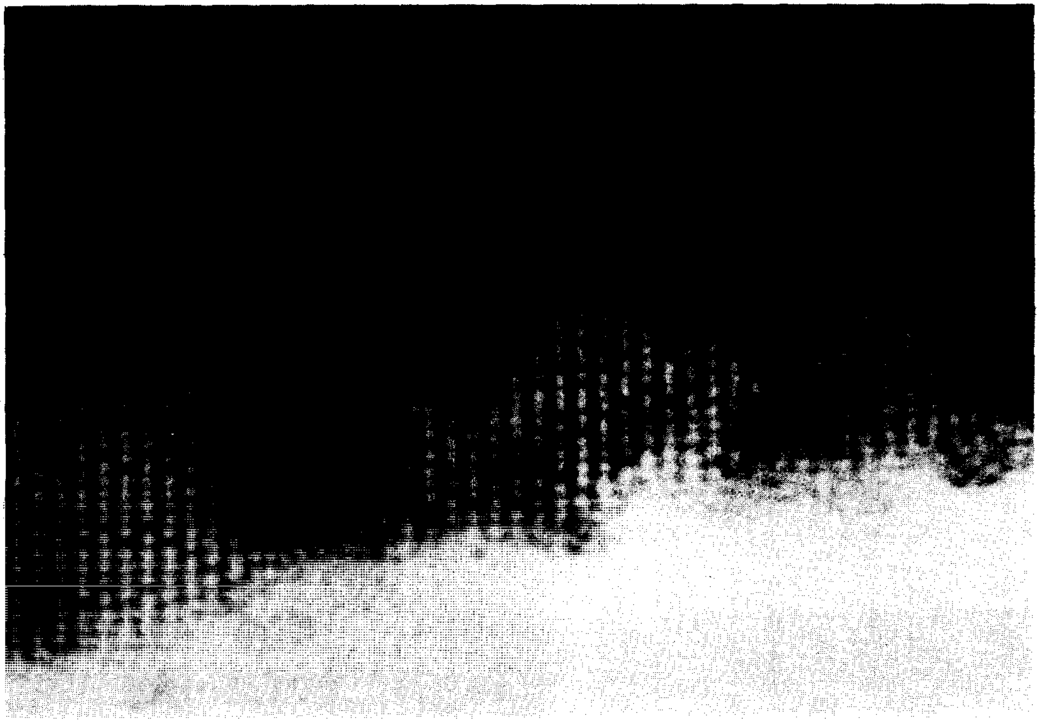

FIG. 11. Isolated (4 × 3) block, $GaNb_{11}O_{29}$, in a matrix of (2 × *n*) blocks.

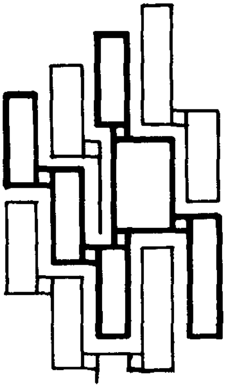

FIG. 12. Structure of encircled region in Fig. 11.

Diffusion, Place Exchange, and Block Growth

Although the atom movements so far described account for the observed structural rearrangements, they do not afford a complete description of the process. Since the reaction proceeds layer by layer, through structures of recognizable composition, a microscopic mass balance can be derived from the initial and final compositions of the transformed region. The initiating step, involving three (2 × 2) blocks, may be written (for the conversion of one layer of cations)

$$\tfrac{3}{2}Ga_2Nb_2O_8 \rightarrow \tfrac{1}{2}Ga_2Nb_8O_{23}.$$

The change of atom populations in the layer transformed is therefore

$$+Nb^{5+} \quad -2Ga^{3+} \quad -\tfrac{1}{2}O^{2-}$$

equivalent to an *efflux* of 2 Ga_2O_3 and an *influx* of Nb_2O_5 per unit of (2 × 5) structure formed. Gallium diffuses outward, under the chemical potential gradient that is established by the volatilization reaction at the surface

$$2Ga^{3+} + 3O^{2-} + 2H_2 \rightarrow Ga_2O + 2H_2O.$$

This outward diffusion is coupled with an inward diffusion of niobium from a surface layer depleted in gallium. At the locus of reaction, there must be a place exchange between gallium and niobium on octahedral sites.

Formation of blocks of other dimensions could take place in two distinct ways.

(A) By a Wadsley–Andersson shift of the *CS* boundaries between blocks. This does not involve any further abstraction of gallium, but must be mediated by a lateral diffusion and place exchange of niobium atoms. That is,

$$\begin{array}{ll} Ga_2Nb_2O_8 + Ga_2Nb_8O_{23} \rightarrow & \\ \quad (2\times 2) \qquad\quad (2\times 5) \quad \rightarrow & \\ & Ga_2Nb_4O_{13} + Ga_2Nb_6O_{18}, \\ & \quad (2\times 3) \qquad\quad (2\times 4). \end{array}$$

Diffusion step: $2Nb^{5+}$.

This mechanism would enable blocks to grow in length at points other than those at which the gallium-abstracting initial step occurs.

(B) As a result of the random occurrence of the initiating atom jump, essentially simultaneously in adjacent blocks. Thus, if unit jumps should occur in adjacent (2 × 2) blocks, four such blocks would be converted, to form a (2 × 3) block and a (2 × 4) block, with one pair of octahedral interstitials

$$\begin{array}{l} 4Ga_2Nb_2O_8 \rightarrow Ga_2Nb_4O_{13} + Ga_2Nb_6O_{18}, \\ \; 4(2\times 2) \;\; \rightarrow \;\; (2\times 3) \qquad\quad (2\times 4). \end{array}$$

Change of atom population: +2Nb −4Ga −O.

It may be noted that, in any of the transformation processes, the number of blocks necessarily changes by 0 or −2, in order that the alternation of cations between the levels $y=0$ and $y=\frac{1}{2}$ should be preserved in the volume-conservative reaction.

It also follows that, as the original (2 × 2) structure becomes extensively replaced by longer (2 × n) blocks, the participation of three contiguous blocks at each transformation step must result in a very rapid increase in block length, culminating in the formation of the R-Nb_2O_5 structure.

In this experiment we have been able to trace the effects of progressively removing Ga_2O_3 from the system Ga_2O_3–Nb_2O_5, within a crystal of $GaNbO_4$ under intense electron beam irradiation. Reaction is highly localized, and is noteworthy in that it proceeds through a succession of hitherto unknown ordered structures, coherently intergrown as domains within the $GaNbO_4$ crystal. These new ordered "compounds" are undoubtedly metastable; the constraints in the system, preservation of coherence and reaction within a constant volume defined by the matrix structure, make the observed sequence of events kinetically favorable, as compared with a fully reconstructive reaction, needed to produce the equilibrium phases.

The mechanism proposed for the reaction involves the cooperative displacement of a pair of cations, with their linking oxygen atom, by $\frac{1}{2}a_R\langle 110\rangle_R$, a fundamental unit jump vector within the ReO_3 structure. Coupled with this initiating step must be atom diffusion and place exchange processes; there is a good deal of evidence from other work on the chemistry of the block structure oxides that such processes are rather facile at high temperatures.

References

1. P. L. Gai and J. S. Anderson, *Acta Crystallogr. A* **32**, 157 (1976).
2. B. F. Pedersen, *Acta Chem. Scand.* **16**, 421 (1962).
3. B. Morosin and A. Rosenzweig, *Acta Crystallogr.* **18**, 874 (1965).
4. H. Brunner and R. Gruehn, *Z. Naturforsch.* **316**, 318 (1976).
5. S. Horiuchi, M. Saeki, and Y. Matsui, *Acta Crystallogr. A* **31**, 660 (1975).
6. P. Gadó, *Acta Phys. Hung.* **18**, 111 (1965).
7. B. G. Hyde and J. S. Anderson, *J. Phys. Chem. Solids* **28**, 1393 (1967).
8. S. Andersson and A. D. Wadsley, *Nature (London)* **211**, 581 (1966).
9. J. M. Browne and J. S. Anderson, *Proc. Roy. Soc. Ser. A* **339**, 463 (1974).
10. M. Sundberg and R. J. D. Tilley, *Phys. Stat. Sol.* (a) **22**, 677 (1974).
11. H. Obayashi and J. S. Anderson, *J. Solid State Chem.* **19**, 331 (1976).
12. S. Iijima, *Acta Crystallogr. A* **31**, 784 (1975).
13. J. S. Anderson, J. L. Hutchison, and J. M. Browne, *Acta Crystallogr. A* **32**, 670 (1976).
14. K. A. Wielhelmi, K. Waltersson, and L. Kihlborg, *Acta Chem. Scand.* **25**, 2675 (1975).
15. J. L. Hutchison, F. J. Lincoln, and J. S. Anderson, *J. Solid State Chem.* **10**, 312 (1974).
16. R. Gruehn, *J. Less-Common Metals* **11**, 119 (1966).
17. J. S. Anderson, J. L. Hutchison, and F. J. Lincoln, *Proc. Roy. Soc. Ser. A* **352**, 303 (1977).