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Crystallization and Ordering of Complex Oxide Structures. I. "Splat-Cooled" Nb_2O_5–TiO_2

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"Splat-cooled" Nb_2O_5–TiO_2 with a melt composition corresponding to $TiNb_{38}O_{97}$ has been examined by high-resolution electron microscopy and electron diffraction. Previous X-ray work showed this material to be crystalline, despite a cooling rate of about 10^5 °C sec^{-1}. The present study reveals a variety of structures ranging from highly ordered block structures to severely disordered regions of uncertain structure and composition. "Double layer" structures are identified, and subtle contrast variations in their crystals are explained in terms of single jogs of overlap structures. Crystallization processes are discussed in the light of these results.

Solidification of melts by ultrarapid quenching methods is of interest not only as a means of producing glassy or noncrystalline solids, but also in the wider context of understanding the transition from the molten to the crystalline state. In an earlier paper (*1*), one of us (A-M.A) described the results of "splat-cooling" experiments on a number of binary systems of refractory oxides, which clearly showed that the ability to form a noncrystalline solid (NCS) is sensitive both to the number of oxygen atoms per cation (NOPC) and to the radius ratio between the two cationic species. In particular, systems involving niobium oxide which, because of their high NOPC, should favor glass formation, ranged in behavior all the way from complete crystallization to the formation of glasses, depending upon the second component. Some of these Nb_2O_5-based systems, which form equilibrium crystal structures of some complexity, lend themselves well to a study of their ultramicrostructure by high resolution electron microscopy and in this paper we report on the ultrastructure of a splat-cooled Nb_2O_5–TiO_2 melt, which was earlier found by X-ray methods to crystallize completely at the highest quench rates. In later papers we shall discuss materials which were previously reported as yielding NCS or as showing partial crystallization.

For present purposes, the significant feature of the Nb_2O_5-based systems is that the melt should deposit equilibrium phases of the so-called block structure type. The material considered here had the composition 95 mole% Nb_2O_5, 5 mole% TiO_2, which corresponds exactly to a known phase $TiNb_{38}O_{97}$, an ordered intergrowth of two files of the $TiNb_{24}O_{62}$ structure (labeled C, Fig. 1) alternating with one file of H–Nb_2O_5 structure (labeled D, Fig. 1) in regular . . . CCDCCDCCD . . . stacking. The large unit cell of this equilibrium structure would have $a = 47.5$, $b = 3.82$, $c = 21.2$ Å, $\beta = 98.5°$. In order that a rather intricate network structure of this kind should be deposited from the melt under nonequilibrium conditions, it would be necessary, during crystallization, to establish and propagate a quite complex pattern of ordering, within which the ordering process can

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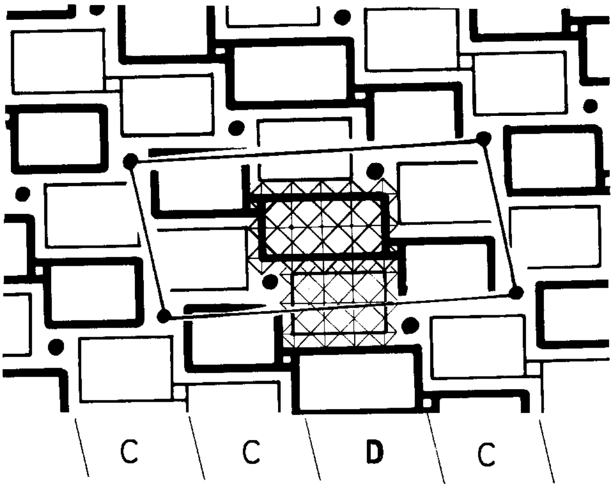

FIG. 1. Structure of $TiNb_{38}O_{97}$, projected along ⟨010⟩.

be broken down into a heirarchy of levels.

(1) One level has deposition at the growth front with the correct nearest-neighbor environment, i.e., with every cation in its appropriate coordination polyhedron.

Duwez (*2*) has argued that if the rate of solidification is sufficiently high, the solid phase can retain the configuration found in the liquid itself; Sarjeant and Roy (*3*) deduced that this would occur only if the quenching rate exceeded some critical value. Little is known about the constitution and properties of molten oxides like Nb_2O_5, but the average coordination number in melts is usually close to that found in the corresponding crystals and molecular dynamics models of simple ionic melts suggest that the local configuration around any ion is mostly a distorted version of the crystalline configuration. In Nb_2O_5-based melts, the growth front is likely to supply cations already furnished with the coordination environment found in the crystal.

(2) Coordination polyhedra immobilized at the growth front could either produce a random network or propagate short-range order by generating elements with the topology of the stable crystal.

In a melt containing both Ti^{4+} and Nb^{5+} cations, the NOPC implies either that some octahedral groups should be linked across edges, as well as through their vertices, or that the coordination number of some cations should be lowered. Edge sharing, which according to Zachariasen (*4*) militates against formation of a random network, makes it possible to build up an element of the block structure crystal, to serve as a viable nucleus for further growth or as an ordered microdomain which may, however, be uncorrelated with its neighbor microdomains. The latter would lead to ultramicrocrystallinity within a randomized total structure.

(3) Local order, once established in a very small region, must propagate itself in one, two, or all three dimensions in order to build up a sizable region of crystalline structure.

If, for materials such as those now considered, crystal growth requires either two-dimensional nucleation or growth around a spiral dislocation, the first nucleus provides a template upon which successive layers of structure are more or less faithfully deposited. In each layer, this replication step not only controls the positions of the atoms but must be chemically selective. We have previously drawn attention to the remarkably good order usually observed along the short axis of block structure crystals, no matter how perturbed in structure and composition is the arrangement within any one layer. This well-established observation is suggestive of an efficient template and replica mechanism.

(4) Attainment of long-range order is a much more stringent requirement.

In general, the stoichiometry of the feedstock will be compatible with more than one variant of the block structure principle; any combination of block sizes, provided that their cross sections permitted fully coherent growth and satisfied the total stoichiometry of the melt, could be built up in the transfer of ions from melt to crystal. Hence the formation of metastable configurations is likely, as isolated units or in more extended domains. They will subsequently be replaced by the equilibrium structure only if readjustments of structure in the actual growth front, or postsolidification changes involving lattice diffusion, can keep pace with the rate of deposition. This requirement is particularly severe in materials such as those discussed here, where the equilibrium state would be a regular stacking of slices of two different crystal structures, differing in composition.

In binary oxide systems, conditions (3) and (4) above both require that, in the growth front, cations should be sorted and assigned to their correct sites. Sarjeant and Roy inferred that the viscosity of the melt and the diffusion rates in the melt are the critical determinants in this process. In the present case, the degree of site specificity, as between Ti and Nb, is rather small, as follows from the structure refinement of $Ti_2Nb_{10}O_{29}$ and $TiNb_{24}O_{62}$ by Cheetham and von Dreele (*5*). Packing mistakes in the growth front—emplacement of a $[TiO_6]$ octahedron in place of an $[NbO_6]$ octahedron or vice versa—are therefore likely and each will impose a change in the medium range ordering and the configuration of blocks around it, because the local ionic charge balance and oxygen/cation ratio are altered. "Wrong" structure initiated by such a mistake locally depletes the melt in one or other component; and must be compensated for by some converse fluctuation of structure and composition as crystallization proceeds.

Processes. As the transformation melt → crystal propagates through the sample, growth processes at the interface will be kinetically controlled both by material transport and by heat transfer. Material transport involves (a) a supply function, for two sorts of cations and determined by the mobilities in the liquid phase and (b) a surface diffusion, on the crystalline phase, that is essential for local ordering by way of migration along terraces and jogs at the edge of the growing layer. If the crystal differs in composition from the melt, one component must be rejected from the growth front, thereby altering the nature of the diffusion barrier on the liquid side of the front. The proclivity to form NCS varies with composition within any one binary system, and this may well be one factor underlying that effect. The rate of heat transfer modifies every step in the process—the sticking probability for ions or coordination groups at the interface, the ionic selectivity, as influenced by surface diffusion, and the residence time of an ion on a surface site, and all diffusion-mediated postdeposition effects and structural readjustments. It is because of their very high rates of heat transfer that the splat-cooling results are of interest.

There is already evidence that attainment of equilibrium ordering, during the crystallization of block structures from the melt, is relatively slow. Structural imperfections and fluctuations of composition have been found in materials solidified at ordinary cooling rates, not exceeding a few hundred degrees per second. In early lattice imaging work Allpress (*6*) observed irregular stacking sequences between H–Nb_2O_5 and $TiNb_{24}O_{62}$ in TiO_2–Nb_2O_5 mixtures solidified from the melt. Iijima (*7*) found isolated elements and domains of the metastable $Nb_{10}O_{25}$ polymorph of Nb_2O_5, with the $(3 \times 3)_1$ block structure, intergrown with the H–Nb_2O_5 structure, after melting pure Nb_2O_5. The work of Allpress and Roth (*8*) has shown how slowly irregularities of stacking are eliminated during prolonged annealing. In our splat-cooling experiments, as reported earlier, the quenching rates were estimated as about 2×10^5 °C/sec; it is therefor not surprising that the product revealed much disorder, the formation of metastable polymorphic structures, and local fluctuations of composition.

Experimental

Preparation of material. The splat-cooling procedure has been described elsewhere (*1*). In brief, the oxide mixture was melted in an argon plasma jet and injected between a pair of fast rotating rollers; these chilled it instantaneously to a wafer a few micrometers thick. The wafer was crushed to provide thin fragments for electron microscopy.

Electron microscopy. The technique of lattice imaging has been adequately described in other papers, and only the relevant details need be given here. Crystal fragments, mounted on "holey" carbon films, were oriented, by means of their diffraction patterns, to bring the short *b* axis parallel to the electron beam. They were examined using a Siemens Elmiskop 102 microscope, at an accelerating voltage of 100 kV, with a high-resolution double-tilt stage. Micrographs were taken at the defocus condition appropriate for optimum phase contrast, and at magnifications up to ×650,000. For some of the niobium oxide structures, including those of concern in this paper, the intuitive contrast associated with thin crystals (<100 Å and approximating to a projected charge density image) is reestablished in much thicker crystals (*9*). This effect was utilized in the present work in assessing disorder along the projection direction.

Results and Discussion

(*1*) *Composition of crystalline material.* All the crystals, identified both by their characteristic (*h*0*l*) diffraction patterns and their lattice images, were found to have compositions in the range $2.480 \leqslant 0/M \leqslant 2.500$, corresponding to $Nb_2O_5 \cdot xTiO_2$, with $0.083 \geqslant x \geqslant 0$. Most of the crystals examined were partly ordered intergrowths of the $TiNb_{24}O_{62}$ and H–Nb_2O_5 structures, with regions displaying fairly well ordered sequences corresponding to $TiNb_{52}O_{132}$ ($MO_{2.4906}$), and $TiNb_{38}O_{97}$ ($MO_{2.4872}$), the made-up composition, as well as domains of both end members of the series. This degree of ordering is illustrated in Fig. 2. Over the whole field of this micrograph, the averaged anion/cation ratio works out at 2.488, remarkably close to the made-up value, 2.487. It is fully recognized that the sampling provided by lattice images cannot necessarily

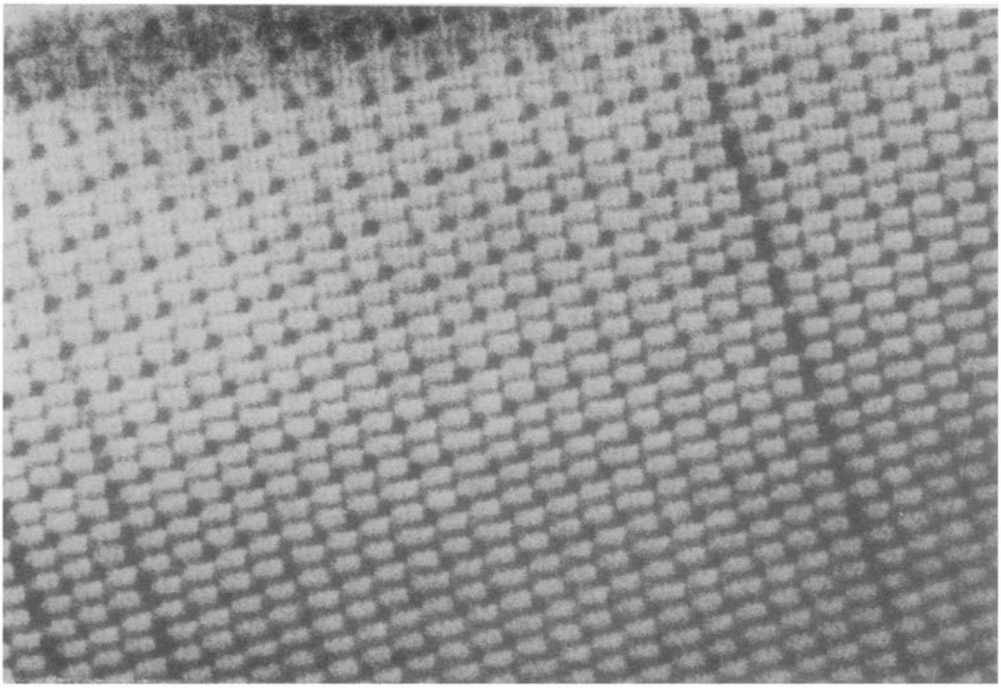

FIG. 2. *h*0*l* lattice image showing intergrown lamellae of $TiNb_{24}O_{62}$ and H–Nb_2O_5. The average anion/cation site ratio in the field shown is 2.488. Note linear "jogs" with overlap contrast.

be taken as representative of the bulk of any specimen, nevertheless, as was demonstrated in work on the system MgF_2–Nb_2O_5 (*10*), the randomness inherent in locating suitable sections for microscopy does give a fair average picture of the chemistry of the system.

(*2*) *Ordered structures.* In such work as this, the question inevitably arises as to how many unit cells of a given structure should be present to justify designation as a discrete "phase." At this level, we prefer to use the term "ordered structure" to denote the regular ordering of a given arrangement of octahedra, over several contiguous repeating units. If the ordered region is sufficiently extensive (e.g., 500 Å in mean breadth), the ordered structure may be unambiguously identified by its contribution to the (often complex) selected area electron diffraction pattern; where ordering is more localized, the evidence is found in the lattice image, as small domains in a more extensive host lattice. Ordered structures identified on this basis are listed in Table I.

$Nb_{10}O_{25}$ is a metastable polymorph of Nb_2O_5, found as small domains in quenched Nb_2O_5 (*7*) and by two of the present authors as an oxidation product of $Nb_{12}O_{29}$ (*11*). At elevated temperatures it transforms to the stable H–Nb_2O_5; the domain of this structure shown in Fig. 3 has been frozen in, the quenching rate being too high to permit of the cation diffusion needed for transformation.

(*3*) *Degree of ordering.* As already stated, many crystals were rather well ordered and uniform in composition. At the other extreme, some crystals gave diffraction patterns too complex to be resolved into one or a few components. Figure 4 shows a lattice image from such a crystal, which shows also the periodic reappearance of projected charge density contrast with increasing thickness; the second area of PCD contrast corresponds to a thickness of about 1000 Å. Domains of ordered structures can be seen in several places: H*–Nb_2O_5 [a recurrently twinned variant of the H–Nb_2O_5 structure earlier found by the authors in vapor-grown crystals of Nb_2O_5 (*12*)], 4 × 4 blocks of the N–Nb_2O_5 structure, in addition to H–Nb_2O_5. Most of the crystal is heavily disordered, however, and in many areas it is evident that disorder extends along the beam direction, as an extensively overlapped structure. This appears as dense black contrast, where empty channels between columns of corner-linked octahedra in some layers overlap octahedral cation positions in other layers. However, the octahedral (and tetrahedral) coordination of the cations is rigorously maintained, as is the "block" character within any one layer. The overlap contrast features are mainly to be found in the thicker regions of crystal, suggesting that they mainly consist of single jogs; the probability of finding a single jog in thin crystal (<100 Å) would be much lower, as is confirmed by the rarity of overlap contrast in thin crystals.

TABLE I

ORDERED STRUCTURES OBSERVED IN "SPLAT-COOLED" $TiO_2 \cdot 19Nb_2O_5$

Structure	Ratio O/M
$TiNb_{24}O_{62}$	2.480
$TiNb_{38}O_{97}$	2.487
$TiNb_{52}O_{132}$	2.491
$Nb_{10}O_{25}$	2.500
$Nb_{16}O_{40}$	2.500
$Nb_{28}O_{70}$	2.500
$Nb_{56}O_{140}$	2.500

(*4*) *Double layer structures.* Some crystals showed evidence of single cooperative jogs over large areas, forming regions of ordered overlap structures. Figure 5 shows a region of H–Nb_2O_5 structure in which a single cooperative displacement has produced an array of "doubled" tetrahedral sites, the contrast within the rectangle arises from the overlap of the structures shown in Figs. 6a, b. Allpress (*13*) has described and identified such features as this, which double the projected tetrahedral sites, but they have not previously been encountered in well-ordered arrays.

(*5*) *Contrast in thin crystals.* Where single jogs are found in thin regions of crystal, one may speculatively interpret the subtle contrast gradations at the tetrahedral sites themselves. Figure 7 contains such a fault, involving the two overlapping structures shown in Fig. 8. Contrast distribution at some of the tetrahedral sites (arrowed) is not symmetrical; this

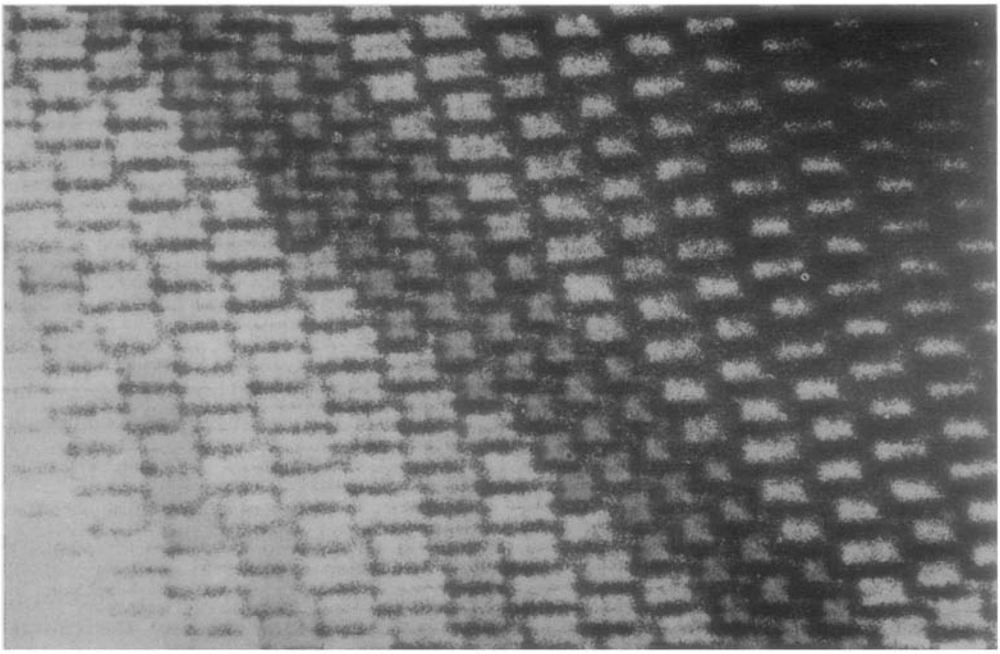

FIG. 3. "Frozen in" domain of $Nb_{10}O_{25}$, in a host structure of $TiNb_{24}O_{62}$ and H–Nb_2O_5. Image contrast in the domain has been enhanced photographically.

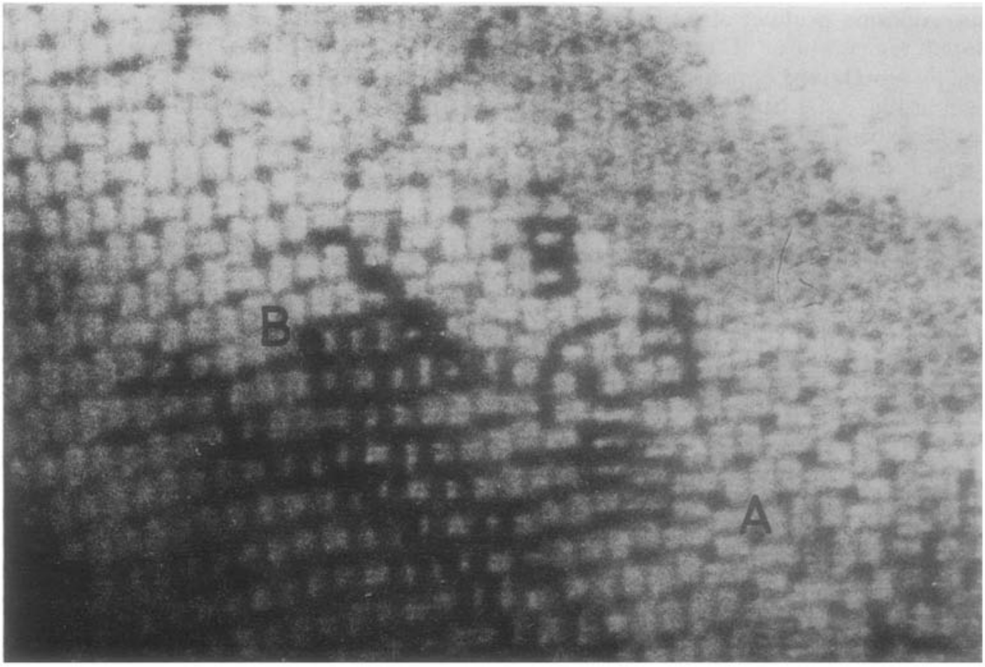

FIG. 4. Severely disordered fragment, containing small domains of H*–Nb_2O_5 at **A** and of N–Nb_2O_5 (4 × blocks) at **B**. Dense black contrast corresponds to extensive block overlap along the *b* axis.

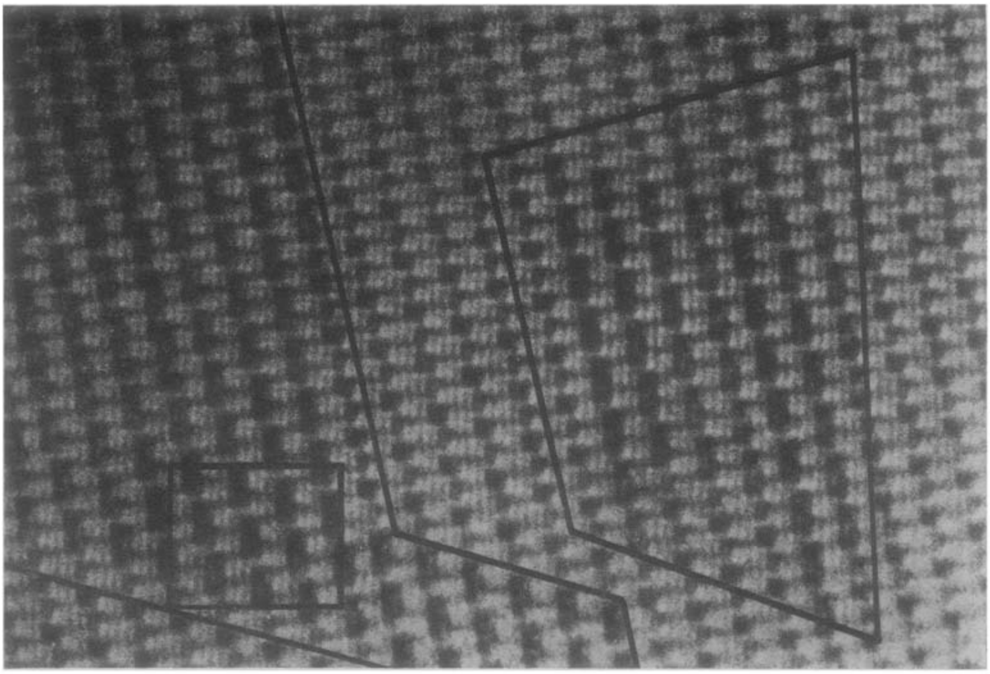

FIG. 5. *h*0*l* lattice image of a region of H–Nb_2O_5, showing a single cooperative slip perpendicular to *b*, generating ordered overlap contrast in outlined areas.

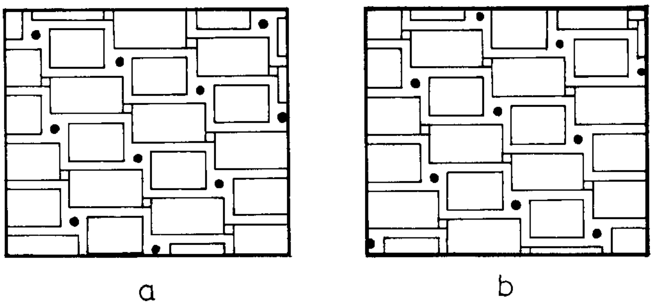

FIG. 6. Two overlapping structures (a) and (b) giving rise to the contrast within the rectangle marked on Fig. 5.

probably arises from the projected overlap of a set of tetrahedral cation positions in one structure with edge-shared octahedra in the overlapped structure. This would destroy the fourfold symmetry of the tetrahedral site, resulting in off-center dark contrast.

This anomalous contrast is quite distinct from the variable tetrahedral site contrast described elsewhere (*14*) and the subject of a recent theoretical treatment by Skarnulis *et al.* (*15*). It has been shown that the filling of cation positions in the square channels at block corners is not simple; extra cations can be incorporated in octahedrally coordinated corner sites (*16*). In thick crystals, all the tetrahedral sites display uniform black contrast, in thin crystals there is a range of contrast from black to white, and the distribution of contrast takes a variety of forms (*14*, *15*).

We suggest that in the thick crystals (>250 layers; see above) there are sufficient tunnel sites to give an averaged filling of every projected site, resulting in uniform dense contrast; for geometrical constraints on such filling,

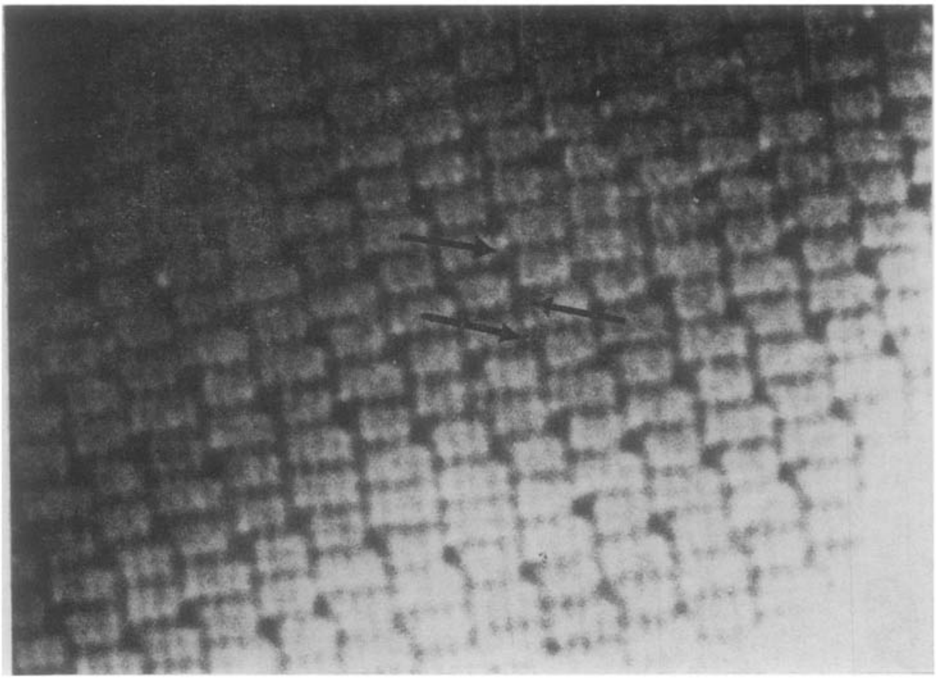

FIG. 7. Thin fragment of H–Nb_2O_5 structure containing a single jog perpendicular to *b*.

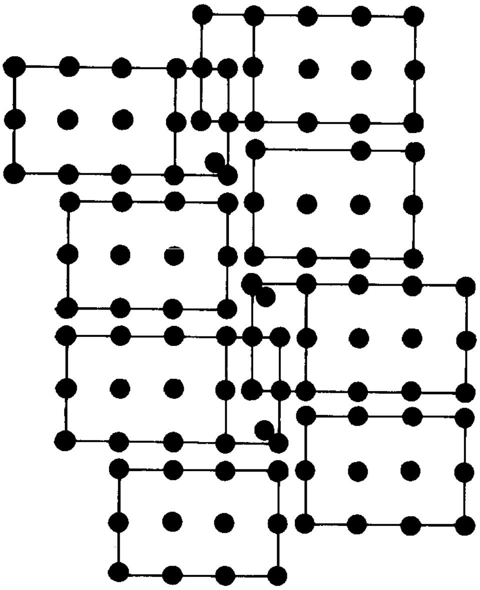

FIG. 8. Projection of overlapping structures in Fig. 7, showing cation positions that give rise to asymmetric contrast at the tetrahedral sites.

see Ref. (*16*). In thin regions, where there are probably less than 25 layers, there is the possibility of an apparently nonrandom distribution which could result in nonuniform image contrast.

As has been discussed, the degree of ordering found in the splat-cooled material varied from point to point within the sample. Over quite considerable volumes, the total composition was close to the average composition of the whole sample, crystals have been built up from elements of the two parent structures, $TiNb_{24}O_{62}$ and H–Nb_2O_5, in the appropriate ratio, even though the long-range order of a 2:1 intergrowth was nowhere maintained over any extensive region. It is noteworthy that none of the other structures in the TiO_2–Nb_2O_5 system (e.g., $Ti_2Nb_{10}O_{29}$) was observed. Since slowly crystallized material also revealed fluctuations of structure and composition (*6*), this result was not unexpected; the scale and extent of the fluctuations reflects the higher rate of solidification in the present experiments. However, other regions of the sample had quite extensive domains of H-Nb_2O_5 structure or its metastable polymorphs, i.e., were free from, or severely depleted in TiO_2. Although rapid, the splat-cooled solidification of a droplet of melt between the chilled rollers is not instantaneous; the rate of heat transfer, and hence the conditions of crystallization, must change as the liquid/solid interface moves from the outside to the center of the thin specimen. Some differential crystallization of the component structures is possible (a) on thermodynamic grounds, if the melt does not have either the eutectic composition or a congruent melting point, or (b) on kinetic grounds, if the rates of nucleation and of subsequent growth differ for the component structures. Information about the melting equilibria in this and similar complex oxide systems is too scanty to judge possibility (a). If Nb_2O_5 crystallized preferentially at any stage, the later crystallate would be enriched in TiO_2 but, as the evidence shows, any enrichment did not proceed beyond the conditions for deposition of $TiNb_{24}O_{62}$. Alternatively, accepting the viewpoint of Duwez (*2*), the most rapidly quenched material, on the outer skin of the wafer, may approximate most closely to the melt and be represented by the regions of correct average composition. In that case, it must in inferred that the $TiNb_{24}O_{62}$ structure was subsequently laid down with some slight preference, to leave a residual liquid enriched in Nb_2O_5, to form the interior of the thin wafer. The way in which specimens must be prepared for microscopy makes it impossible to judge whether a given fragment comes from the outer or inner parts of the original specimen, and the problem of sequential or preferential crystallization during ultrarapid cooling must therefore be left open.

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