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Intermediate Phases and Pseudophases in the System WO_3–Nb_2O_5: Tetragonal Tungsten Bronze Phases

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Ordered intermediate phases with finely graded compositions are found in the Nb_2O_5–WO_3 system: homologous series of crystallographic shear phases for x in MO_x (M = Nb + W) > 2.9; a succession of block structures and intergrowth structures for $2.5 \leqslant x \leqslant 2.65$. The intermediate range has pentagonal tunnel structures partly based on the tetragonal tungsten bronze network. Ordered filling of some rational but variable, fraction of tunnel sites, in principle, could generate a new closely graded series of phases. Synthetic experiments and lattice imaging electron microscopy have been applied to this system. At least for the experimental conditions employed, the structure of the congruently melting $4Nb_2O_5 \cdot 9WO_3$, with 4/12 of pentagonal tunnels occupied, dominates the stability field. However, structures with 6/16 sites in a 2 × 2 TTB superlattice, and with 7/20 sites in a 5 × 1 TTB superlattice occupied form quite extended domains in a $4Nb_2O_5 \cdot 9WO_3$ matrix. In addition, the structure with 5/16 sites in a 2 × 2 TTB superlattice forms domains in preparations richer in WO_3 than $4Nb_2O_5 \cdot 9WO_3$, and this $2Nb_2O_5 \cdot 5WO_3$ structure itself shows evidence of ordered intergrowth with the $2Nb_2O_5 \cdot 7WO_3$ characterized electron microscopically by Iijima. The status of these ordered domain structures is discussed. Metastable structures may be effectively stabilized by coherent intergrowth with structures that are absolutely stable.

Introduction

Detailed structural studies of oxide systems have disclosed a variety of mechanisms whereby a succession of ordered intermediate phases can be formed, with finely graded compositions, in place of, and more stable than, truly nonstoichiometric, thermodynamically bivariant solid solutions. Recurrent crystallographic shear, coherent intergrowth, and superlattice ordering are three such mechanisms. The possibility of variable patterns of ordering peculiar to tunnel structures (e.g., the hollandite structure and the tetragonal tungsten bronzes) has not hitherto been thoroughly explored. We report here experiments designed to examine whether a closely spaced series of compounds can exist in the tetragonal tungsten bronze structure based upon differing fractional occupation of tunnel sites.

The essential feature of tunnel structures is that variability of composition can arise only from changes in the fractional occupancy of tunnel sites within an invariable framework. X-ray crystal structure determinations (e.g., on a derivative of the tetragonal tungsten bronze type (*1*)) in several instances have yielded fractional occupancy ratios, but this does not necessarily connote that sites within any one tunnel are only partially occupied. It could equally well arise from a statistically random distribution of fully occupied tunnels or from domains in antiphase relation, or with different ordering patterns and compositions, within a locally well-ordered crystal. Direct information on local structure is needed to resolve this problem, and we have used the electron microscopic lattice imaging method, already successfully applied to tetragonal tungsten bronze structures by Iijima and Allpress (*2*, *3*).

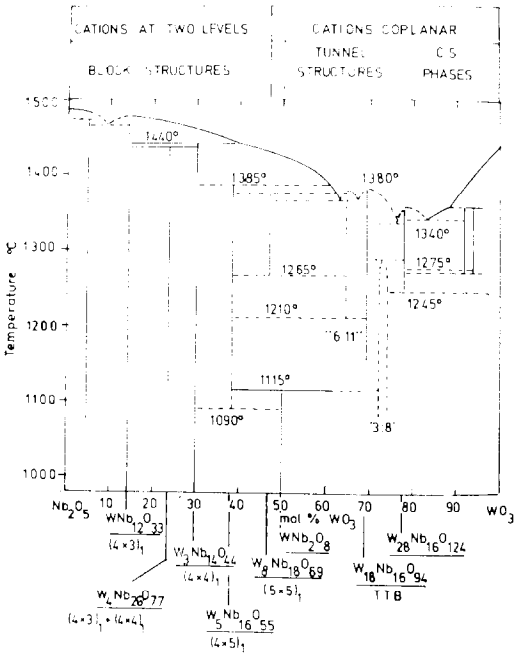


FIG. 1. Equilibrium diagram of the system Nb_2O_5–WO_3.

Roth and Waring (*4*), using thermal analysis and X-ray diffraction methods, showed that there is a very rich progression of intermediate phases in the system WO_3–Nb_2O_5 (Fig. 1).

All these phases are structurally related; topologically they form a family of polyhedron network structures in which the ReO_3 structural type (represented, in distorted form, by WO_3) is modified as the *oxygen*:*total metal* ratio is progressively lowered by replacing W(VI) by niobium (V). The network of octahedra adapts itself by traversing three successive structural types. For small degrees of substitution (3 to 8 mole% Nb_2O_5), change of stoichiometry is accommodated by crystallographic shear (*5–8*). At the niobium rich end (100–53 mole% Nb_2O_5) is a succession of block structures (*9*, *10*). Between these ranges are structures based upon pentagonal tunnels, which comprise an uncertain number of compounds related to the tetragonal tungsten bronzes. Throughout the system there is the possibility of adaptive ordering to form numerous intermediate phases by changes in the orientation and spacing of *CS* planes, or by variation in column cross sections and formation of coherent intergrowths in the block structures (*11–13*).

Roth and Waring already indicated that analogous phase successions may exist in the pentagonal tunnel compounds. The only

TABLE I

COMPOSITIONS EXAMINED FOR POSSIBLE TUNNEL ORDERING IN TTB STRUCTURES

Molar ratio Nb_2O_5:WO_3	Mole fraction Nb_2O_5	Superlattice multiplicity relative to simple 12 × 12 Å bronze	Tunnel occupancy ratio	Formula of crystallographic unit cell	Observed
6:11	0.353	2 × 1	3/8	$\{(NbO)_3Nb_9W_{11}O_{60}\}_n$	Intergrowth
14:29	0.326	5 × 1	7/20	$\{(NbO)_7Nb_{21}W_{29}O_{150}\}_n$	Intergrowth
22:47	0.319	4 × 2	11/32	$\{(NbO)_{11}Nb_{33}W_{47}O_{240}\}_n$	—
4:9	0.308	3 × 1	4/12	$\{(NbO)_4Nb_{12}W_{18}O_{90}\}_n$	Stable
26:61	0.299	5 × 2	13/40	$\{(NbO)_{13}Nb_{39}W_{61}O_{300}\}_n$	—
2:5	0.286	2 × 2	5/16	$\{(NbO)_5Nb_{15}W_{25}O_{120}\}_n$	Intergrowth[a]
3:8	0.273	5 × 1	6/20	$\{(NbO)_6Nb_{18}W_{32}O_{150}\}_n$	Intergrowth
2:7	0.222	(2 × 2)[b]	—	$\{(NbO)_{12}Nb_{12}W_{28}O_{120}\}$	Not prepared

[a] Intergrowth with the 2:7 structure and with 4:9 TTB.
[b] Hybrid of ReO_3 and TTB structure types.

unambiguously defined compound is the congruently melting $9WO_3 \cdot 4Nb_2O_5$, $(NbO)_4$-$Nb_{12}W_{18}O_{90}$; this has 4 out of 12 tunnels occupied in a 3×1 superlattice of the simple tetragonal bronze. The tunnels are occupied by –O–Nb–O–Nb–O– strings (niobium in pentagonal bipyramidal coordination) and it is likely that any occupied tunnel is completely filled. Another phase, at about 35 mole% Nb_2O_5, stable to high temperatures and also assigned a 3×1 tetragonal tungsten bronze unit cell, has been variously formulated as $11WO_3 \cdot 6Nb_2O_5$ (*4*), $24WO_3 \cdot 13Nb_2O_5$ (*9*), and $7WO_3 \cdot 4Nb_2O_5$ (*14*). There is also a phase at about 25 mole% Nb_2O_5, for which no ordered superlattice was found, which unmixes at high temperatures into $9WO_3 \cdot 4Nb_2O_5$ and $7WO_3 \cdot 2Nb_2O_5$ (now identified as $(NbO)_4$-$Nb_{12}W_{28}O_{120}$, (*2*)).

As guiding principles in the design of preparative experiments, we assumed: (1) that discrete ordering patterns can arise from the occupation of some rational fraction of pentagonal tunnels; (2) that (cf. *2*, *3*) there may be restrictions on the occupation of closely adjacent tunnels; (3) that the resulting crystallographic repeating units will not necessarily be restricted to the 3×1 superlattice of the bronze structure. In addition, the known phase diagram indicated that experiments could be restricted to systems with 35 ± 5 mole per unit of Nb_2O_5. On this basis, the compositions shown in Table I were investigated. In Table I, compositions are shown in Cols. 1 and 2. For superlattices of the 12×12 Å tetragonal bronze framework, as indicated in column 3, these compositions result from the ordered occupation of the fraction of tunnels shown in Col. 4. Included in Table I, but not prepared in this work, is the mixed tetragonal bronze–ReO_3 type structure, $7WO_3 \cdot 2Nb_2O_5$.

Experimental

Sample preparation. Samples were prepared from Johnson Matthey Specpure Nb_2O_5 and WO_3, blended and finely ground in the proportions indicated in Table I. The mixtures were heated in sealed silica capsules. The usual heating schedule was at 800°C for 140 h, then at 1050°C for 90 h, and finally at 1250°C for 94 h, the sample being ground up and thoroughly remixed between successive heatings. The 1250°C anneal was omitted in the case of the 22:47 mixture. Because of its importance in Roth and Waring's phase diagram, the 6:11 sample was prepared several times by slightly different methods. Typical heating schedules were at about 800°C for 140–150 h, and at 1000–1050°C for 48–90 h, in silica, followed by annealing for 65–94 h at 1300°C in a sealed platinum capsule.

The products were examined by X-ray diffraction, using a Hägg–Guinier camera with Cu$K\alpha$ radiation.

Electron microscopy. The principal method of investigation was by direct lattice imaging electron microscopy, the procedures of which have been discussed elsewhere (e.g., *15*, *16*). Materials were finely ground and dispersed on carbon films and examined with a Siemens Elmiskop 102 microscope, at 100 kV, using a high-resolution goniometer stage. Thin crystal flakes (<100 Å thick) were oriented so that [001] was exactly parallel to the electron beam, and micrographs were recorded at about 900 Å underfocus, using all diffracted beams out to about 0.35 $Å^{-1}$.

In these conditions, the image contrast approximates closely the projected charge density in the crystal and corresponds to the position of the heavy (W and Nb) atoms, as projected down the short axis of the structure, one octahedron in depth. Allpress and Iijima (*2*, *3*) showed that the rather complex image of the tetragonal tungsten bronze structure lends itself to unambiguous interpretation. The clusters of heavy atoms at filled pentagonal tunnels are not resolved (resolution 3.5 Å) and show as heavy disks of contrast; empty pentagonal tunnels show as white dots. In conjunction with the constraints imposed by the creation of pentagonal tunnels in groups of four, by rotary shear of the ReO_3 parent structure (*17*), these features enable the real structure to be mapped. The essential problem then is only to recognize the order displayed in the distribution of filled tunnel sites.

Results and Discussion

The 6:11, 14:29, 22:47, 26:61, and 2:5 preparations. For all these preparations, the

lattice images unexpectedly corresponded closely to that of the 4:9 structure (referred to later). In most cases, the crystals were either very heavily twinned or showed a high degree of randomness in tunnel occupancy.

Figure 2 shows a representative micrograph, obtained from the 22:47 preparation. The structure is highly faulted, but the 36 × 12 Å unit cells of the 4:9 type, in two orientations, can be traced over most of the area shown, and the averaged occupancy of tunnels, over both ordered and faulted areas, is found to be close to 0.333. The image must therefore be taken as that of an incompletely annealed stage of ordering in the 4:9 structure.

In general, the faulting is due only to irregularity in the distribution of occupied pentagonal tunnels; the skeletal framework of tetragonal tungsten bronze structure is almost always perfect. A rare instance of faulting in the framework is shown in Fig. 3a; the outlined area is analyzed in Fig. 3b. This is a stoichiometric fault: The composition of the fault band is the same as that of the rest of the crystal. Across a "slip band" $\frac{1}{2}a$ wide (18 Å), the structure has been displaced by a total of $\frac{1}{3}b$ (4 Å), and two contributions to this displacement can be recognized. (a) In the perfect TTB structure, centers of rotational shear that derive the TTB structure from the

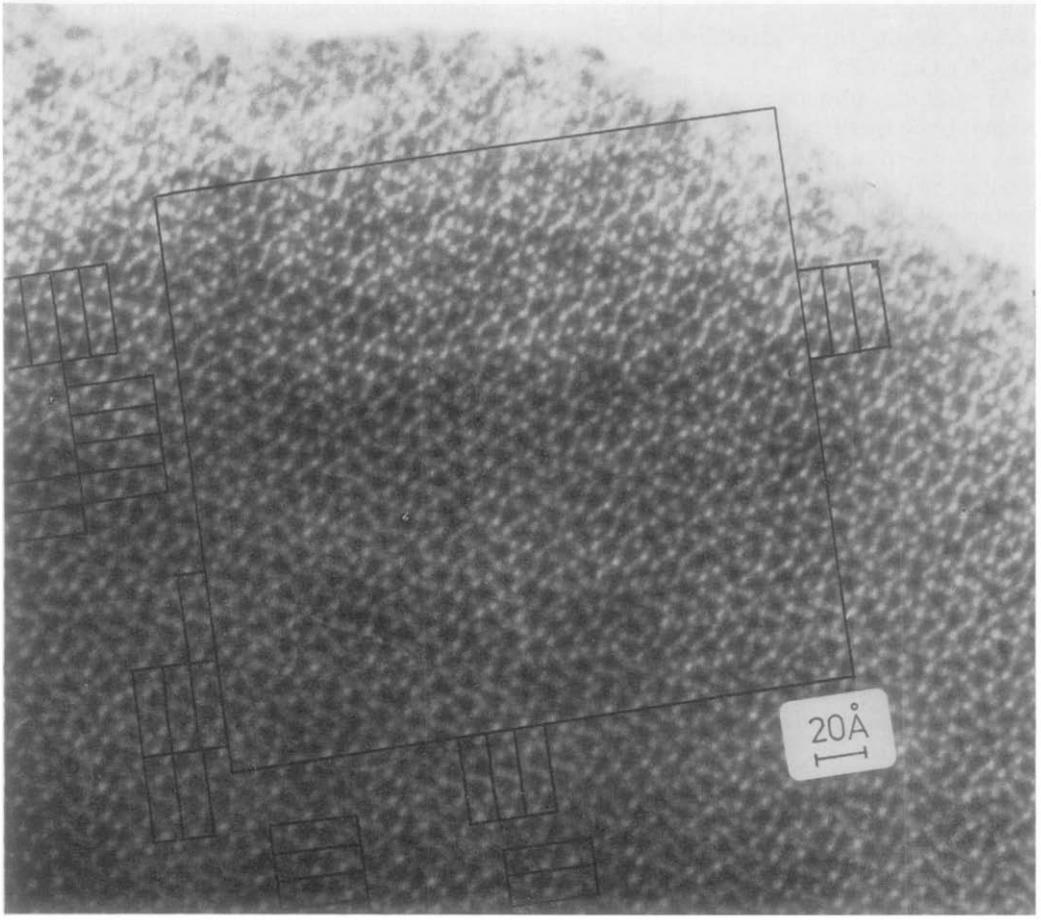


FIG. 2. Irregular filling of pentagonal tunnels observed in the 22:47 preparation. Local regularity conforms to the 4:9 structure; a few 36 × 12 Å unit cells of this, in two orientations, are marked. Average tunnel occupancy in the outlined region is 0.332.

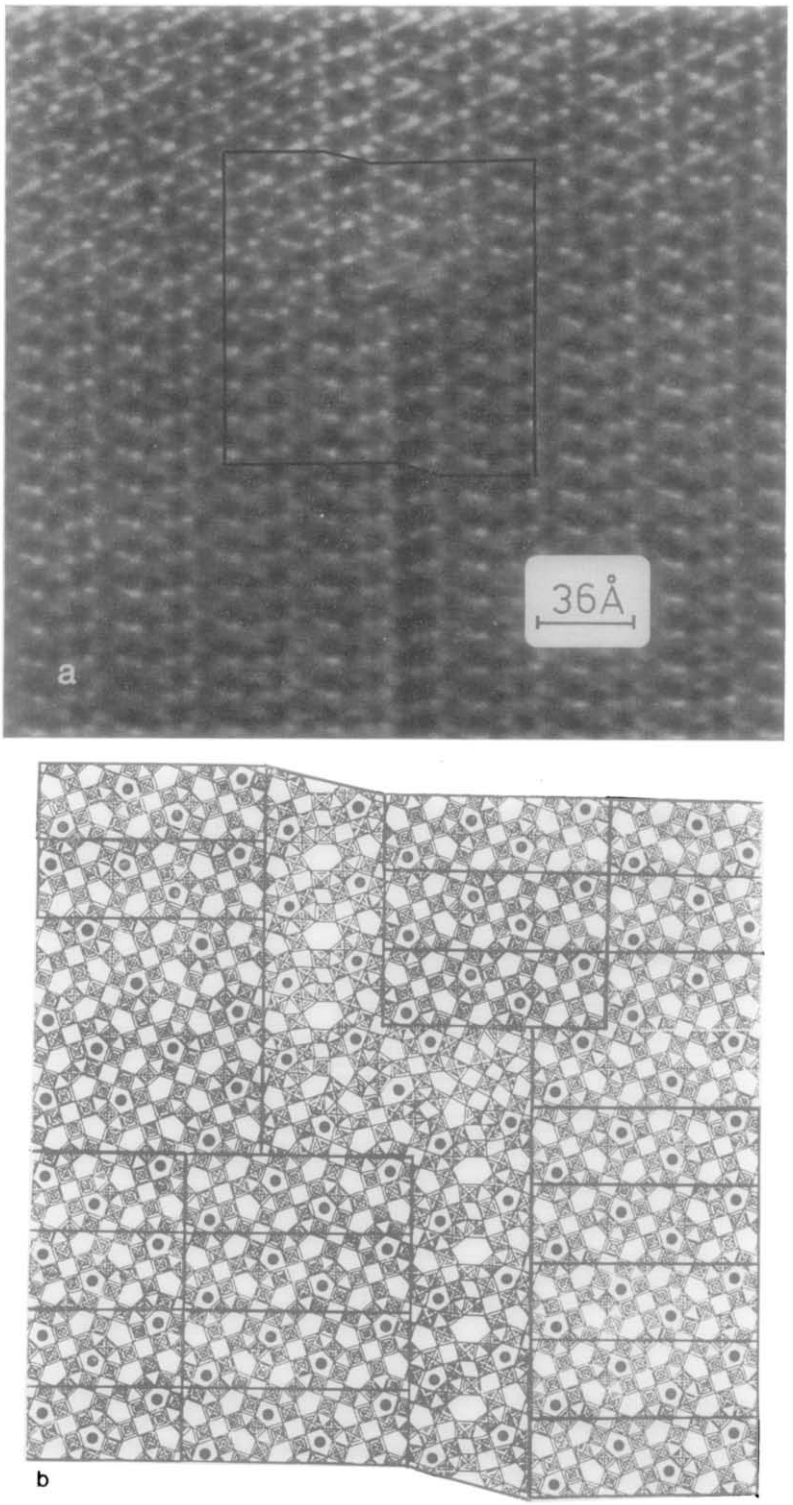
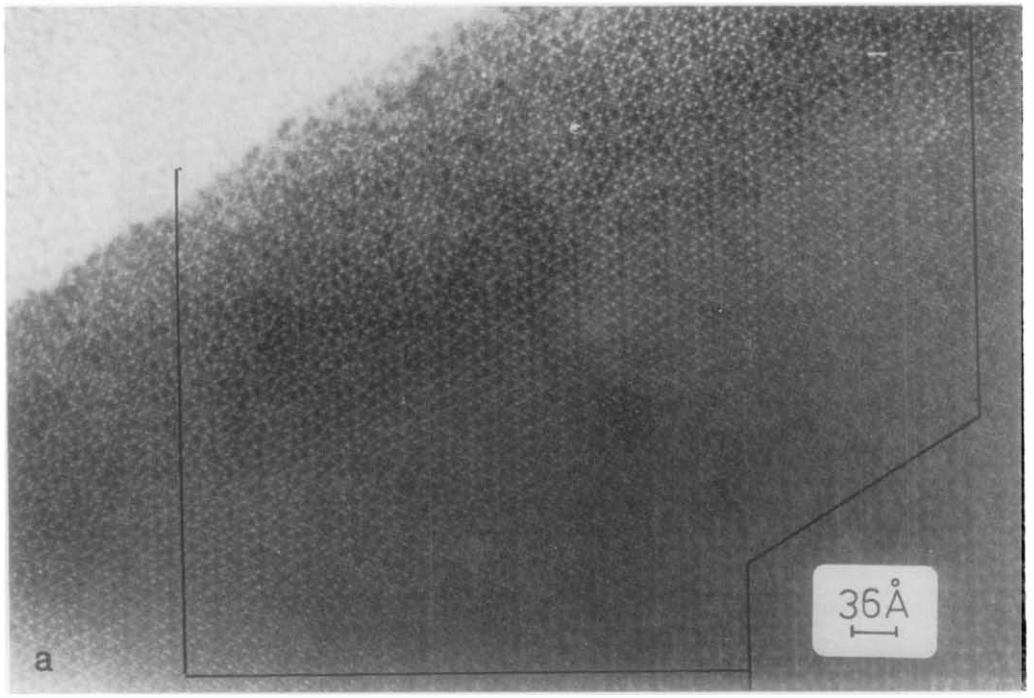


FIG. 3. (a) Slip band in TTB host structure, observed in the 2:5 preparation. (b) Analysis of the outlined region of (a), showing the empty hexagonal tunnel running along (001).



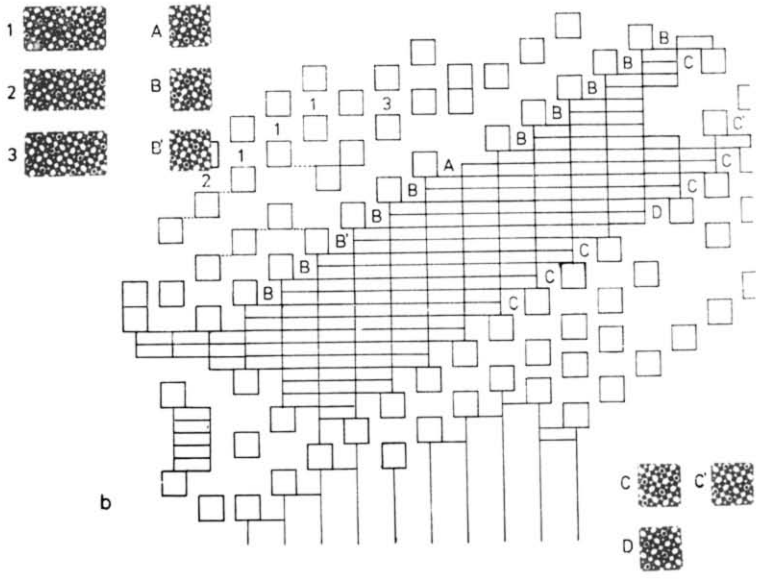


FIG. 4 (a). Fluctuation of composition within the 3:8 composition, showing coherent intergrowth of the 4:9 and 2:5 structures, and regular coherent intergrowth between 2:5 and 2:7 structures (composition 6:17). (b) Analysis of structure of the outlined region in (a). Squares (24 × 24 Å) represent unit cells of 2:7 compound; rectangles (36 × 12 Å) represent unit cells of 4:9 structure. Local compositions: areas 1, 2, 3, B, and C, 2:5; A and D, 2:7. (c) Structure of $2Nb_2O_5 \cdot 7WO_3$.

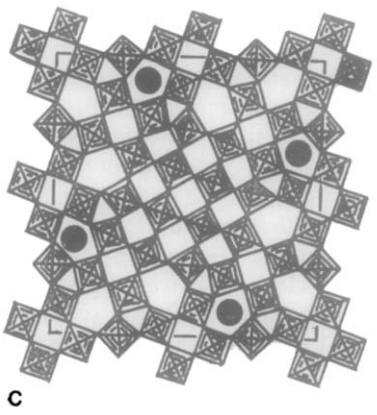


FIG. 4 (c).

ReO_3 parent type and that lie on any [100] line are all of the same sense. Across the slip band, their sense is reversed. (b) The antiphase relation resulting from this would displace the structure by $\frac{1}{2}b$ across the fault, but would impose very severe distortions on the octahedra in the slip band. These are partially relieved by a relaxation of $-\frac{1}{6}b$, giving the total displacement observed. As can also be seen, a slip band of this kind can side step coherently by a integral multiple of the sub-units of the TTB structure; in this case the jog measures two units ($\frac{2}{3}a = 24$ Å). The out of phase relationship between the domains on either side of the slip band creates a set of hexagonal tunnels, one of which, at the sidestep, is occupied. Hexagonal tunnels have not hitherto been observed in the Nb_2O_5–WO_3 system, although they are known in the hexagonal tungsten bronzes (*18*), tin tungsten bronzes (*19*), and molybdenum–oxide system (*20*).

The 3:8 preparation. The possible existence of a 3:8 compound was predicated on the hypothesis that 6/20 of the pentagonal tunnels could be occupied in a 5×1 TTB super lattice (60×12 Å). In fact, a new structural type emerged, which indicated that the 3:8 composition falls into the transition between ReO_3 and TTB structural types.

A representative micrograph is shown in Fig. 4*a* and is analyzed in Fig. 4*b*. This lattice image corresponds to a mixture of three structures, coherently intergrown in a TTB framework: (i) the 4:9 true TTB structure; (ii) the 2:7 structure of Iijima and Allpress (Fig. 4c); (iii) a new type that may be designated at "2:5" structure. The region shown clearly includes a fluctuation of composition within the specimen, which caused the mixture of structures to develop, but particular interest attaches to the tungsten-richer parts, on both sides of the strip of ordered 4:9 TTB structure.

In these parts, elements of two distinct structures can be recognized, both based on a 24×24 Å square cell (i.e., a 2×2 superlattice). One of these, denoted by empty squares, is the 2:7 hybrid of the ReO_3 type with pentagonal tunnels. The other has the unchanged TTB framework, with 16 pentagonal tunnels in the unit cell, of which 5 are occupied. The composition is thus $(NbO)_5Nb_{15}W_{25}O_{120}$:$2Nb_2O_5 \cdot 5WO_3$. Occupation of 5/16 tunnels necessarily confers a low symmetry on the arrangement; there is some randomness in the way tunnel sites are occupied, as is shown by the variants B,B′,C,C′. Of these, configuration *B* and its mirror image *C* occur most frequently and probably represent the most stable arrangement. Similar variations are to be seen where (as in the spaces marked 1, 2, 3) pairs or longer arrays of these 2:5 cells are adjacent. In a few places (e.g., A, D), only 4/20 of the tunnels are occupied; the resulting composition must be $(NbO)_4Nb_{12}W_{28}O_{120}$, a defective alternative structure for the 2:7 composition. Nowhere have we found extended areas of the 2:5 structure; on the available evidence it appears to be a stoichiometrically defined metastable structure, stabilized by formation from and intergrowth with the 4:9 host structure. Other examples of this intergrowth-stabilized, metastable ordering have been found by electron microscopy, and we may term such structures pseudocompounds.

Of particular interest, however, is the rather well-ordered way in which the unit cells of the compound are arranged in a matrix of the 2:5 structure. The pentagonal tunnel elements of the 2:7 structure provide for perfect continuity of the TTB framework, so that fully coherent intergrowth is possible. In the area mapped, the intergrowth approximates to a regular 2:1 intergrowth of 2:5 with 2:7, i.e.,

a net Nb_2O_5:WO_3 ratio of 6:17. The lamellae of intergrowth form a good boundary along [210] of the 4:9 TTB structure. Conditions under which the regular intergrowth phase could be prepared in a pure state have not so far been found.

This part of the equilibrium diagram merits more extensive work. Coherent intergrowth between the 4:9 TTB and 2:5 pseudocompound, and between the 2:5 and 2:7 structures, in principle, could lead to a closely spaced succession of phases which would be difficult to characterize by X-ray diffraction methods. The metastable phase in Roth and Waring's phase diagram, which they tentatively designated the "3:8" compound, falls into this region and may well be either a regular intergrowth or a textured mixture of the 4:9 and 2:5 (or 6:17) structures.

The 4:9 phase $(NbO)_4Nb_{12}W_{16}O_{90}$. The microstructure of melt-grown 4:9 compound has been studied by Iijima and Allpress. Figure 5, a micrograph of annealed 4:9 compound confirms that a high degree of perfection is attained in the ordering process. We have also examined the product of the solid-state reaction between the 9:8 phase ($W_8Nb_{18}O_{69}$, 5×5 block structure) and WO_3 at lower temperatures (1200°C for 24 h), in the expectation that intermediate stages in the reaction, with a higher Nb_2O_5:WO_3 ratio, might be disclosed. Lattice images, exemplified by Fig. 6a showed several types of intergrowth, including the 6:11 and 14:29 structures. Such coherent intergrowths are shown in the area analyzed in Fig. 6b. Their presence lends weight to the initial hypothesis that alternative rational modes of tunnel filling should be attainable, although the experimental conditions for preparing defined homogeneous materials have not been found.

The 4:9 crystal shown in Fig. 6a is twinned across (310), as is commonly the case. Around the twin boundary, the scheme of tunnel

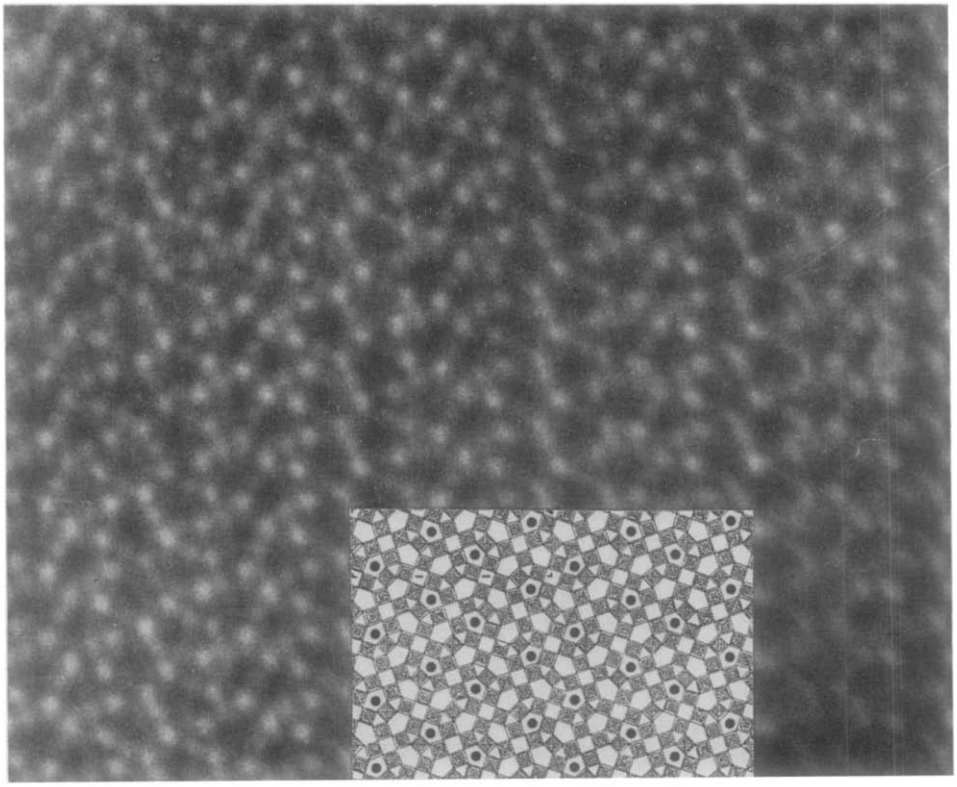


FIG. 5. Lattice image of well-ordered $4Nb_2O_5 \cdot 9WO_3$, with crystal structure superposed.

occupancy is much less regular and corresponds to an enrichment in Nb_2O_5. In Fig. 6b, the unlabeled strips represent perfectly ordered arrays of 4:9 structure, in the two orientations. In the filler strip EFG, irregular in shape but based on the 12 Å square module to preserve continuity of the host framework, there is no order in the tunnel occupancy; the fractional

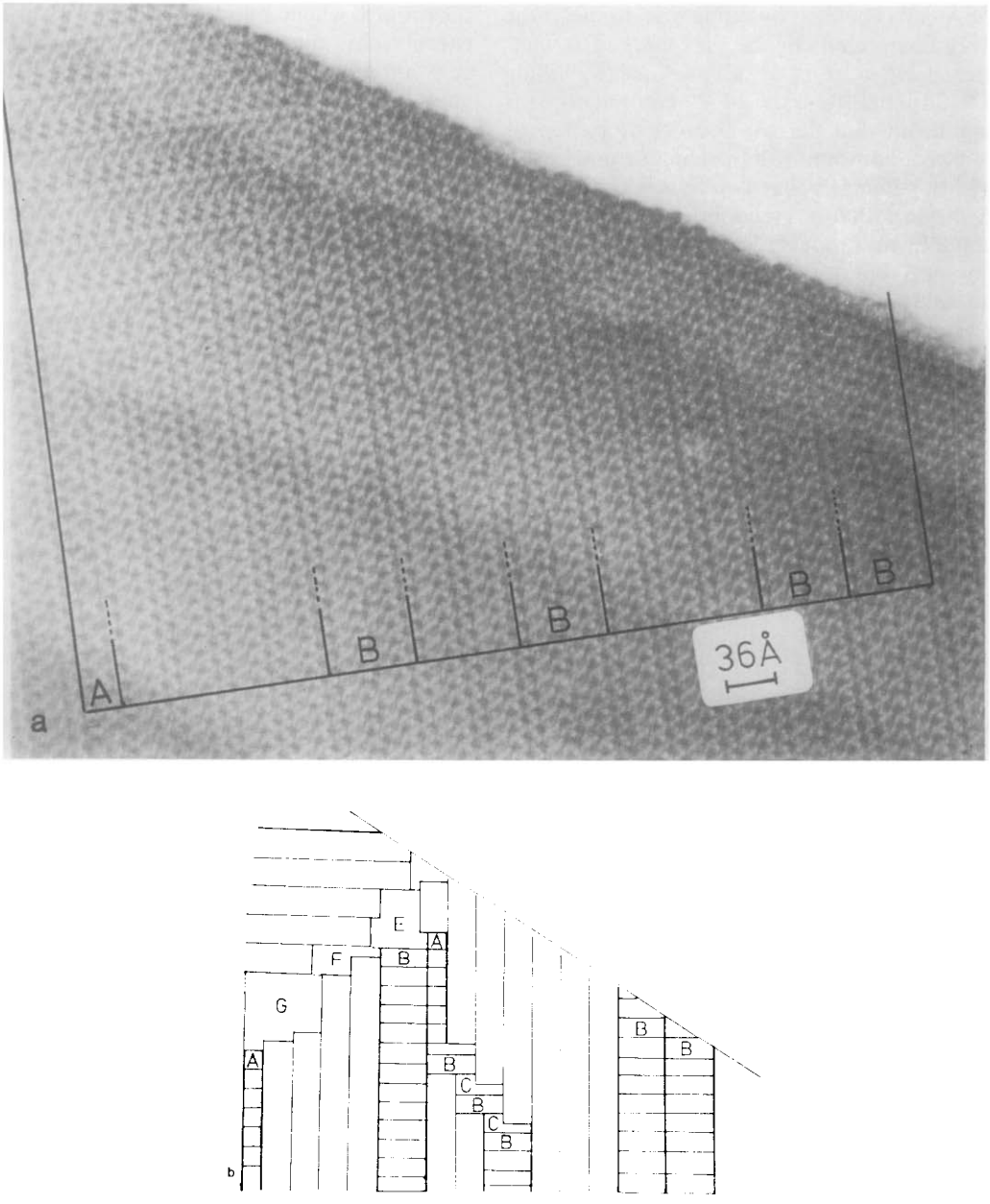


FIG. 6. (a) Coherent intergrowth of 6:11 and 14:29 compositions with 4:9 structure. (b) Analysis of structure in the outlined region of (a). Rows of unit cells marked A, B correspond to the 6:11 and 14:29 ordering patterns respectively. Occupancy of pentagonal tunnels in disordered regions C, D, E, F, and G is 0.357, 0.350, 0.336, 0.368, and 0.350, respectively.

occupancy ratios are 0.336, 0.368, and 0.350 in E, F, and G respectively. Running right across the field of the micrograph, however, are several rows of new, perfectly ordered structures. In the two files marked A, a 24 × 24 Å cell is defined by filling 6/16 tunnels: the 6:11 compound. In the files marked B, cells measuring 60 × 24 Å are defined by filling 13/40 tunnel sites: the 14:29 compound. It is significant that the 14:29 ordering pattern is to be found not only as a strip one unit cell in width, but as lamellae two cells wide. It might be argued that a single-unit strip such as A could be an artefact: local order accidentally imposed on a faulted region between two domains of good crystal. That this 14:29 ordering pattern holds throughout a region 120 Å wide and of indefinite length is good evidence that it represents a distinctive structural arrangement, which may well be capable of attainment throughout larger domains.

Discussion

This study serves to emphasize the stability of the congruently melting 4:9 TTB structure, which presumably optimizes the interactions between occupied pentagonal tunnels. The randomness frequently observed, both in this work and in that of Iijima and Allpress shows that these order-controlling interactions are relatively weak. They can, in preparations with a lower *oxygen*:*metal* ratio, impose alternative ordering patterns, as is shown by the formation of the postulated 6:11 and 14:29 structures as intergrown lamellae. It is an open question whether these represent thermodynamically stable structures which, by suitable preparative methods, could be obtained as homogeneous materials; it is, alternatively, possible that metastable structures can be stabilized as lamellar intergrowths. Figure 7 shows schematically the free energy-composition relations in a system A–B with a large number of closely spaced intermediate, crystallographically defined structures. The locus of their free energy minima lies close to the free-energy curve of a hypothetical nonstoichiometric solid solution. Compound X is absolutely stable, and coexists with phase W at a defined chemical potential μ_{WX} of component B; the species $Y, Z \ldots$ are metastable. Y and W could coexist at practically the same chemical potential as X and W. However, because the phases are closely spaced on the composition axis, the chemical potential at which X and Y could coexist as the equilibrium phase pair may differ very substantially from the stable equilibrium value μ_{WX}. The thermodynamics of the system is determined by the W–X coexistence criteria, but for some composition C close to X the nett increase in free energy of the system will be raised only by a small amount if some structure corresponding to the notional phase Y is built into the crystals as a "solute" in X as "solvent."

The part of the Nb_2O_5–WO_3 phase diagram richer in WO_3 than the 4:9 compound also presents new features of some interest. There are clear indications that an ordered structure is possible with 5/16 of the tunnels filled but, as with the 6:11 and 14:29 structures, it has not been established whether this forms a stable equilibrium phase. The evidence that this tunnel filling arrangement can form intergrowths with, and perhaps be stabilized by, the hybrid 2:7 structure suggests that the entire WO_3-rich side of the equilibrium diagram is potentially of the "adaptive order" type (*21*). In this composition range there is a succession of type structures, all derived from the ReO_3

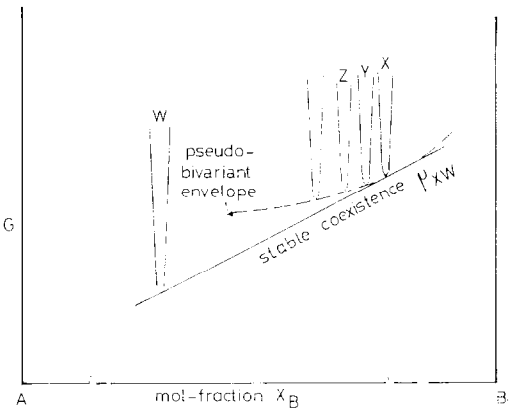


FIG. 7. Schematic free energy-composition diagram, showing close succession of phases X, Y,Z . . . simulating nonstoichiometric behavior. X and W coexist in stable equilibrium; Y is just metastable but can be kinetically stabilized by intergrowth with X.

type and all with a framework of coplanar cations, which is topologically capable of generating a continuous range of intergrowth structures.

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