# Electron Microscopy of the Niobium Oxides. Part II.[1] Multiple Phases in the System $Nb_2O_5$ + $MgF_2$

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The formation of mixed phases in the system $MgF_2$ + $Nb_2O_5$ has been examined, on the grounds that similarity in ionic radii between Mg and Ti, and between F and O, should lead to the analogues of the known titanium–niobium block structure oxides. Electron diffraction and direct electron microscope lattice imaging methods show that, in addition to the compound already described as $MgNb_{14}O_{35}F_2$, with the $(5 \times 3)_\infty$ structure, phases isostructural with H-$Nb_2O_5$, N-$Nb_2O_5$, $TiNb_{24}O_{62}$, and $Ti_2Nb_{10}O_{29}$ are formed. By compensatory substitution, each of these structures represents a solid solution series and mixtures with compositions on the $MgF_2$–$Nb_2O_5$ tie line yield multiphase products. Regular intergrowth structures may be formed between the basic structural types.

PREVIOUS studies[1,2] have shown the power of electron microscopy in elucidating structural detail, at the unit cell level, in niobium oxide and some of its derivatives. In this paper the method is used to map the chemistry and the phase relationships in the system $MgF_2$ + $Nb_2O_5$ and to study the nature of the disorder encountered in the structures observed.

In 1961 Wadsley demonstrated that cations of different valency could be substituted for $Nb^{5+}$ cations in octahedral sites to generate mixed oxides that preserved the structural principles found in H-$Nb_2O_5$. Thus in the system $TiO_2$–$Nb_2O_5$ he identified a number of distinct phases. Two of these, $TiNb_2O_7$[3] and $Ti_2Nb_{10}O_{29}$[4] (the structures of which are shown schematically in Figure 1) could be classified as members ($m = 3$ or 4) of a homologous series with the general formula $M_{3m}O_{8m-3}$.

The structures are of the 'block' type, with rectangular columns of corner sharing $[MO_6]$ octahedra (*i.e.*, $ReO_3$ type) spliced together at two levels and of infinite extent along the *b* axis of the crystal. In the two examples cited, adjacent columns at the same level are linked into infinite ribbons by further octahedron edge sharing. The block structure of $TiNb_2O_7$ can therefore be symbolised as $(3 \times 3)_\infty$; that of $Ti_2Nb_{10}O_{29}$ as $(4 \times 3)_\infty$. No other member of this homologous series has been found in the $TiO_2$–$Nb_2O_5$ system, but in the series $M_{3m+1}O_{8m-2}$ [to which H-$Nb_2O_5$ ($Nb_{28}O_{70}$) also belongs] there is the phase $TiNb_{24}O_{62}$, $(4 \times 3)_2$, and the regular 1 : 1 intergrowth $TiNb_{52}O_{132}$ [$= (4 \times 3)_2 + (4 \times 3)_1 + (5 \times 3)_\infty$] is also known.

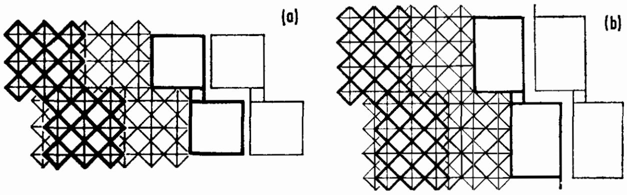

FIGURE 1 Idealized structure of (a) $TiNb_2O_7$ $(3 \times 3)_\infty$ and (b) $Ti_2Nb_{10}O_{29}$ $(3 \times 4)_\infty$; [010] projection

$MgF_2$ is isostructural with $TiO_2$ and the ionic radii are similar: $Mg^{2+}$, 0·66 Å; $Ti^{4+}$, 0·68 Å; $Nb^{5+}$, 0·69 Å; $O^{2-}$, 1·32 Å; and $F^-$, 1·33 Å (1 Å = 0·1 nm). Formation of mixed phases may therefore be possible and, indeed, one such phase has been characterized by its crystal structure as a $(5 \times 3)_\infty$ block structure, the $m = 5$ member of the homologous series, and assigned the composition[5] $MgNb_{14}O_{35}F_2$. This has no known

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[1] Part I, J. S. Anderson, J. M. Browne, and J. L. Hutchison, *J. Solid State Chem.*, 1972, **5**, 419.

[2] J. G. Allpress, *Mat. Res. Bull.*, 1969, **4**, 707; S. Iijima, *Acta Cryst.*, 1973, *A* **29**, 18.

[3] A. D. Wadsley, *Acta Cryst.*, 1961, **14**, 660.

[4] A. D. Wadsley, *Acta Cryst.*, 1961, **14**, 664.

[5] M. Lundberg, *J. Solid State Chem.*, 1970, **1**, 463.

counterpart in the pure oxide systems. As is shown below, the chemistry of the $MgF_2$–$Nb_2O_5$ system is more complex than this, and the presence of both cations and anions in two valence states leads to complexities in the coexistence and coherent intergrowth of solid solutions of several structural types.

## EXPERIMENTAL

Mixtures of Johnson–Matthey ' Spec-Pure ' $MgF_2$ and $Nb_2O_5$ were mixed in the molar ratios 1 : 1, 1 : 3, 1 : 5, 1 : 7, 1 : 14, 1 : 22, 1 : 26, and 1 : 50. They were annealed in sealed platinum tubes for periods of up to one week at successive different temperatures of 1000 °C, 1300 °C, and 1380 °C. The tubes were weighed before and after heating and in most cases virtually no loss of material was detected.

Samples were prepared for electron-microscope examination by techniques described elsewhere and examined in a JEM 100-U electron microscope. For identification purposes, crystals were sought which could be oriented with their *b*-axes parallel to the electron beam; with the limitations imposed by the use of a 10° tilting stage, only a relatively small number of fragments from each sample could be identified in terms of a ' type structure ' (as discussed later). Where suitably oriented crystals were also sufficiently thin, lattice images were recorded, at a magnification of *ca.* 250,000×. At an appropriate amount of defocus[6] it was possible to show a direct correlation between the lattice image and the actual structure, and in this way complex intergrowths and disordered regions could be analysed in detail.

## RESULTS

*Classification of Structures and Compositions of Samples.*—Most of the crystal fragments brought into a suitable diffracting orientation could be classified as belonging to one or other of the simple, basic structure types listed[7-9] and exemplified in Table 1. These structures have related, but distinctive ($h0l$) electron diffraction patterns, and the identifications were made on the basis of these characteristic patterns by use of selected area diffraction, crystal by crystal. Lattice images frequently revealed domains of coherent intergrowth between different structures, and yielded information about disordered structures. On the working hypothesis that the anion : cation ratio of a crystal is substantially identical with its crystal formula, *i.e.*, that point defects in these materials are insignificant, the generalized formulae of individual crystals, or of small domains, can thus be identified. Actual compositions cannot be ascertained, however, since each structure type corresponds to a potentially wide range of solid solution (see below).

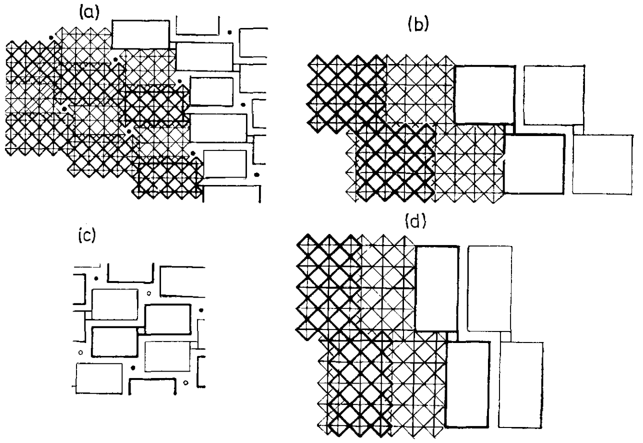

FIGURE 2 Structures of (a) H-$Nb_2O_5$, (b) N-$Nb_2O_5$, (c) $M_{25}X_{62}$, (d) $M_{15}X_{37}$ in Table 1; ' Structure types '

TABLE 1

Basic block structure types

| X : M ratio | Structure | Compounds | Lattice parameters $a$/Å | $b$/Å | $c$/Å | β | Ref. |
|---|---|---|---|---|---|---|---|
| 2·500 | $M_{28}X_{70}$ | H-$Nb_2O_5$ | 21·16 | 3·82 | 19·35 | 119·8° | 7 |
| 2·500 | $M_{16}X_{40}$ | N-$Nb_2O_5$ | 28·50 | 3·83 | 17·48 | 124·8 | 8 |
| 2·480 | $M_{25}X_{62}$ | $TiNb_{24}O_{62}$;<br>$Nb_{25}O_{62}$ | 29·7 | 3·82 | 21·2 | 94·9 | 9 |
| 2·468 | $M_{15}X_{37}$ | ' $MgNb_{14}O_{35}F_2$ | 20·7 | 3·82 | 19·1 | 107·7 | 5 |
| 2·417 | $M_{12}X_{29}$ (Monoclinic) | $Ti_2Nb_{10}O_{29}$;<br>$Nb_{12}O_{29}$ | 20·5 | 3·81 | 15·6 | 113·7 | 4 |

A recognised problem in the chemical applications of electron microscopy is that the samples studied may be unrepresentative, owing to inadequate mixing, segregation, or selective fracture of crystals. In only a few instances has this question been examined. It therefore appeared important to get some statistical check that valid inferences could be drawn from the observations, so *ca.* 250—300 crystals were examined and identified from $h0l$ sections. For each mixture $MgF_2$ + $r Nb_2O_5$, and for each set of annealing conditions, the total number of fragments observed to have each of the structures was recorded. From these sparse statistics, representing only a small proportion of each sample, an observed average composition was calculated. Since the results showed that no phase analogous to $TiNb_2O_7$ is formed, the $MgF_2$ could not be fully incorporated into block structure compounds from mixtures with small $r$. When this is taken into account, the general agreement between the ' observed ' total anion : catio ratio and the made-up composition of the bulk sample was surprisingly

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[6] J. L. Hutchison and J. S. Anderson, *Phys. Stat. Solidi*, 1972, (*a*) **9**, 207.

[7] B. M. Gatehouse and A. D. Wadsley, *Acta Cryst.*, 1964, **17**, 1545.

[8] S. Andersson, *Z. anorg. Chem.*, 1967, **351**, 106.

[9] R. S. Roth and A. D. Wadsley, *Acta Cryst.*, 1965, **18**, 724; R. Norin, M. Carlsson, and B. Elgquist, *Acta Chem. Scand.*, 1966, **20**, 2892.

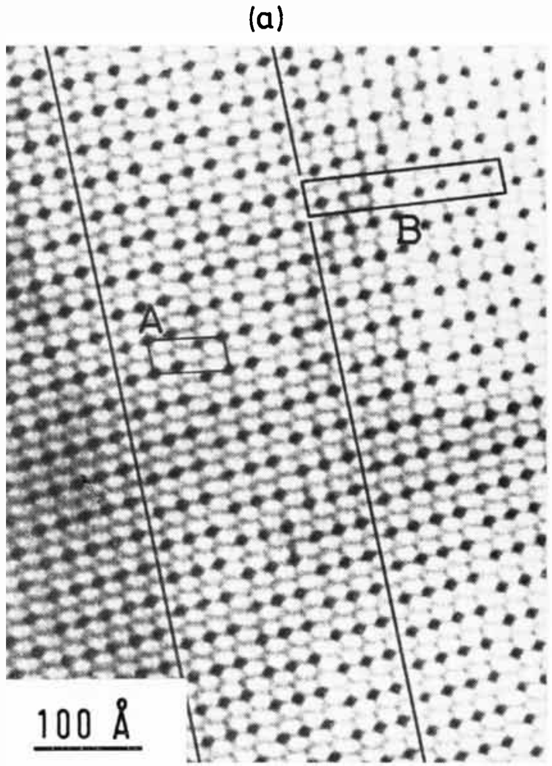

PLATE 1 Lattice image of C,D rows with unit cells of $M_{39}X_{97}$ (region ' A ') and $M_{103}X_{256}$ (region ' B ') outlined. Dark dots define tetrahedral sites

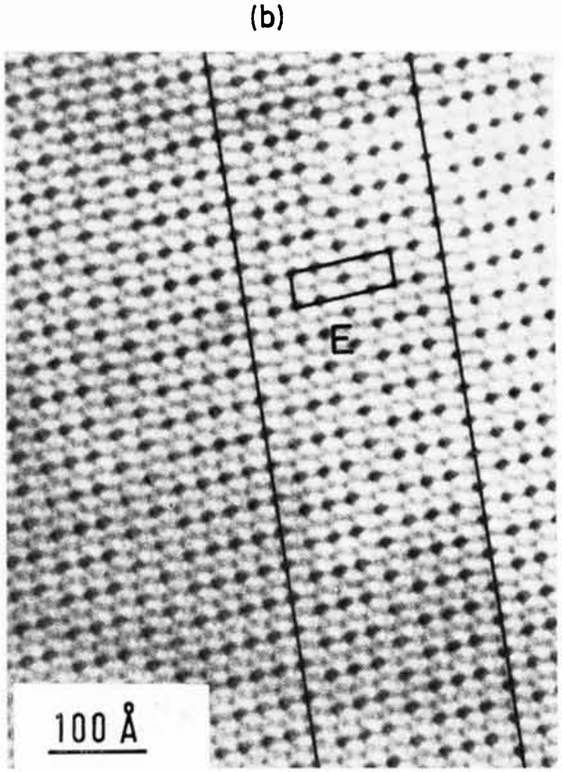

PLATE 2 Lattice image of C,D rows showing domain of Norin's suggested $M_{53}X_{152}$ cell (outlined) region ' E '

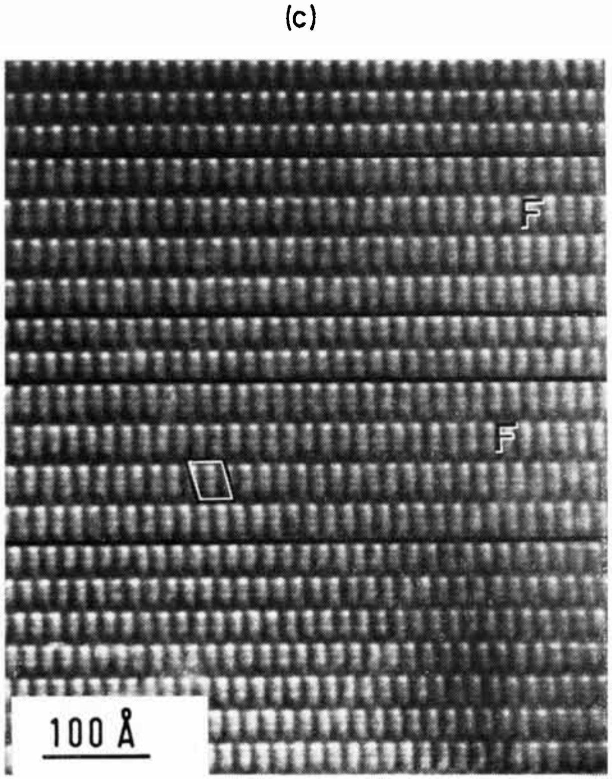

PLATE 3 Lattice image of domain of $M_{18}X_{45}$ in $M_{15}X_{37}$ (region ' F ')

good (Tables 2 and 3). It may be inferred that the microscopy afforded a fairly reliable guide to the structures or phases present in well annealed samples, and therefore to the chemistry of the system.

TABLE 2

Structures present in $MgF_2 + r Nb_2O_5$ mixtures annealed at 1000 °C for 160 h. Number of sample fragments possessing indicated structure-types

| $r$ | $M_{12}X_{29}$ | $M_{15}X_{37}$ | $M_{25}X_{62}$ [a] | $M_{28}X_{70}$ | $M_{16}X_{40}$ | Composition Theor. | Composition Obs. |
|---|---|---|---|---|---|---|---|
| 1 | | 2 | | | 3 | 2·330 | 2·485 |
| 3 | | 1 | | | | 2·430 | 2·490 |
| 5 | | 6 | | | 5 | 2·450 | 2·481 |
| 7 | | 15 | | | 15 | 2·467 | 2·480 |
| 14 | 1 | | | | 7 | 2·480 | 2·475 |
| 22 | 2 | 6 | | | 9 | 2·490 | 2·490 |
| 26 | | 4 | | 1 | 10 | 2·490 | 2·500 |
| 50 | 1 | | | 13 | | 2·495 | 2·500 |

[a] No single-structured crystals of this type identified by electron diffraction patterns, but coherently intergrown domains in other host structures frequently observed.

TABLE 3

Structures present in $MgF_2 + r Nb_2O_5$ mixtures annealed at 1300 °C for 160 h. Numbers of sample fragments possessing indicated structure-types

| $r$ | $M_{12}X_{29}$ | $M_{15}X_{37}$ | $M_{25}X_{62}$ [a] | $M_{28}X_{70}$ | $M_{16}X_{40}$ | Composition Theor. | Composition Obs. |
|---|---|---|---|---|---|---|---|
| 1 | | 6 | | | | 2·33 | 2·467 |
| 3 | | 5 | | | | 2·43 | 2·467 |
| 5 | | 12 | | | | 2·45 | 2·467 |
| 7 * | 6 | | | | | 2·467 | 2·417 |
| 14 | 11 | 11 | | 5 | | 2·480 | |
| 22 * | 3 | | | 9 | | 2·490 | 2·480 |
| 26 | | 1 | | 3 | 8 | 2·490 | 2·490 |
| 50 | 3 | | | 8 | | 2·495 | 2·495 |

[a] See footnote *a* of Table 2.

* Annealed at 1380 °C.

Tables 2 and 3 show that a variety of structures was observed for each sample, both as discrete crystals and, as discussed below, in the form of coherently intergrown domains of different structure within individual crystals. The compositions corresponding to these structures differed from that of the initial mixture; a multiphase equilibrium is involved, which gives rise to a different distribution between phases when the samples are annealed at higher temperatures. It is not appropriate to treat the $MgF_2 + Nb_2O_5$ mixtures as a pseudo-binary system: one is concerned with a particular section of the four-component system (Nb,Mg)(O,F). The choice of components to represent the equilibria is to some extent arbitrary, but in view of the constraint that mixtures were prepared along the pseudo-binary tie line $MgF_2$–$Nb_2O_5$, it is instructive to consider the experimental findings in terms of reciprocal pairs of species, based on the process (1). The product

$$Mg_{\frac{1}{2}}F + NbO_2O_{\frac{1}{2}} \rightleftharpoons Mg_{\frac{1}{2}}O_{\frac{1}{2}} + NbO_2F \qquad (1)$$

structures are strictly defined in terms of total anion : cation ratios, but since there are both anions and cations in two different charge states, compensatory substitution can generate a range of solid solutions from each structure type, with the generalized formulae shown in Table 4, column 4. In the formally analogous system $TiO_2$–$Nb_2O_5$, where no compensation is possible, each structure corresponds to a closely defined composition.

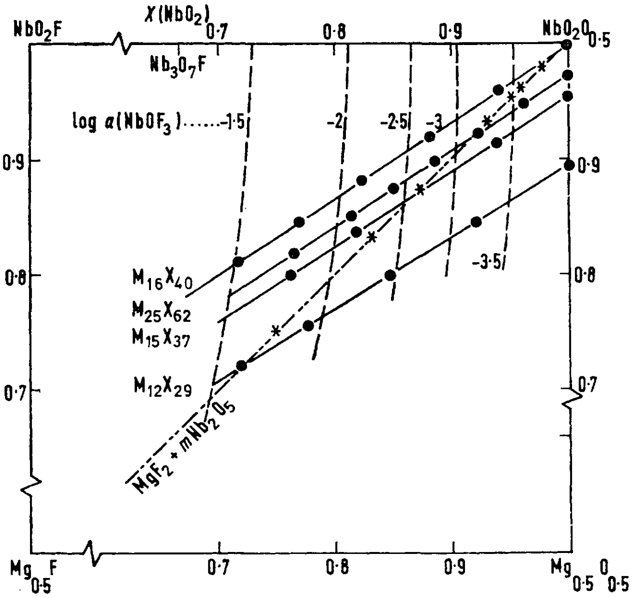

FIGURE 3 Phase diagram for reciprocal pair $NbO_2F$–$Mg_{0·5}O_{0·5}$, showing compositions of 'made up' $MgF_2 + Nb_2O_5$ in relation to the solid solution structures observed. Fine dashed lines represent contours of equal activity of $NbOF_3$

TABLE 4

Solid solution series in $MgF_2$,$Nb_2O_5$

| Structure type | $TiO_2$ member | $MgF_2$ analogue | General formula | Limit |
|---|---|---|---|---|
| $M_{28}X_{70}$ | — | — | $Mg_xNb_{28-x}O_{70-3x}F_{3x}$ | $Nb_{28}O_{70}$ |
| $M_{16}X_{40}$ | — | — | $Mg_xNb_{16-x}O_{40-3x}F_{3x}$ | $Nb_{16}O_{40}$ |
| $M_{25}X_{62}$ | $TiNb_{24}O_{62}$ | $MgNb_{24}O_{60}F_2$ | $Mg_xNb_{25-x}O_{63-3x}F_{3x-1}$ | $Mg_{1/3}Nb_{24\,2/3}O_{62}$ |
| $M_{15}X_{37}$ | — | $MgNb_{14}O_{35}F_2$ | $Mg_xNb_{15-x}O_{38-3x}F_{3x-1}$ | $Mg_{1/3}Nb_{14\,2/3}O_{37}$ |
| $M_{12}X_{29}$ | $Ti_2Nb_{10}O_{29}$ | $Mg_2Nb_{10}O_{25}F_4$ | $Mx_xNb_{12-x}O_{31-3x}F_{3x-2}$ | $Mg_{2/3}Nb_{11\,1/3}O_{29}$ |

Figure 3 shows the resulting equilibrium diagram. Compositions of the several solid solutions fall on lines of constant structure type, which have as their origins the ternary compounds lying on the line for which [F] = 0 (Table 4, column 5).[10] Phases of rational composition, such as $MgNb_{14}O_{35}F_2$, represent only particular compositions within these solid solution ranges, and do not necessarily imply any regular and distinctive distribution of atoms over the sites of the anion and cation sublattices. Points corresponding to phases with integral numbers of fluorine atoms per formula unit are marked on each line.

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[10] R. Norin and B. Dahlen, *Acta Chem. Scand.*, 1969, **23**, 1826; A. Burdese, M. L. Bolera, and P. Rolando, *Atti Accad. Sci. Torino*, 1964, **99**, 565.

Table 4 shows that only the compositions $MgNb_{24}O_{60}F_2$, $MgNb_{14}O_{35}F_2$, and $Mg_2Nb_{10}O_{25}F_4$ lie on the pseudobinary tie line; other structures and compositions imply that the components are distributed independently between the products of reaction by the intervention of some species that does not lie on the pseudobinary tie line. It can readily be shown that the various solid solution series can be converted into one another by gain or loss of $Nb_3O_7F$ which, through reactions (2) and (3) can redistribute Nb, O, and F

$$3Nb_3O_7F \rightleftharpoons NbOF_3 + 4Nb_2O_5 \qquad (2)$$

$$5NbOF_3 \rightleftharpoons 3NbF_5 + Nb_2O_5 \qquad (3)$$

through a vapour-transport process. In the four-component system, therefore, three solid phases, assignable to the solid solution series, can coexist, with compositions related through the constraint that the activity of the volatile species (*e.g.*, $NbOF_3$) is constant.

Although thermodynamic information is completely lacking, the relation between the compositions of coexisting phases can be crudely estimated as follows. If we make the gross approximation that the reciprocal pair system can be treated as a regular solution, we can assign mole fraction concentrations $X_{NbO_2}$, $X_{mg}$, $X_o$, and $X_F$ (where mg and o represent $Mg_{0·5}$ and $O_{0·5}$ respectively) and, for convenience set $X_{NbO_2} + X_{mg} = X_o + X_F = 1$. Then we obtain equation (4) and (neglecting the temperature dependent scaling factor

$$p(NbOF_3) = K\,\frac{X_{NbO_2} \cdot X_F{}^3}{X_o{}^2} \qquad (4)$$

*K*) we can calculate $p(NbOF_3)$ as a function of *X* for each of the solid solution phases. On Figure 3 are marked derived contours of constant $p(NbOF_3)$, which afford some indication of the coexistence tie lines between solid solutions of different structures.

In general terms, the observed phase compositions are compatible with this reasoning: the made-up compositions do not represent single phases, but are the mean compositions of phase assemblies lying along an activity contour. It follows that the (stable) H-$Nb_2O_5$ and (high-temperature metastable) N-$Nb_2O_5$ structures that frequently recur need not be those of the pure oxides $Nb_{28}O_{70}$ and $Nb_{16}O_{40}$, but may also contain Mg and F. It can also be noted that not only is the coherent intergrowth of three structures within any crystal thermodynamically permitted, but that domain growth may be complex. It is not clear that normal phase-rule considerations can be applied to coherent intergrowth systems; in a number of cases[11] their behaviour has suggested an additional degree of freedom arising from the extensive variables that are usually subsumed in an interfacial energy between domains of different structure.

*Structures identified by Lattice Imaging*.—Several domains which were too small to generate electron diffraction patterns were identified from their lattice images. One of the structures thus identified was similar to one of the (Ti,Nb) intergrowth oxides; the others were hitherto unreported structures: (i) $M_{39}X_{97}$. Allpress[12] described the compound $TiNb_{38}O_{97}$ in terms of regularly intergrown lamellae of the H-$Nb_2O_5$ (D-rows) and $TiNb_{24}O_{62}$ (C-rows) structures. The ordered sequence . . . CCDCCDCCD . . . gave the complex formula $TiNb_{38}O_{97}$. The monoclinic unit cell had dimensions $a = 47·5$, $b = 3·82$, $c = 21·2$ Å, $\beta = 98·5°$, as shown in Figure 4(a). Plate 1 shows a lattice image of a crystal, consisting of rows of $M_{25}X_{62}$ structure (C-rows) with lamellae of $M_{28}X_{70}$ (D-rows) structure (arrowed). The region ' A ' is a domain containing the recurrent sequence . . . CCDCCD . . . as in the analogous Ti,Nb mixed oxide. The structure type of this region is $M_{39}X_{97}$ and it has the general formula $Mg_xNb_{39-x}O_{98-3x}F_{3x-1}$.

(ii) $M_{53}X_{132}$. Gruehn and Norin[13] obtained a well characterized niobium oxide $NbO_{2·483}$ which they recognized, from *X*-ray powder diffraction evidence, as a non-stoicheiometric (metal excess) regular intergrowth compound between H-$Nb_2O_5$ and $Nb_{25}O_{62}$, *i.e.*, ideally $Nb_{53}O_{132}$. They suggested that the stacking sequence in the intergrowth was . . . CCDDCCDD . . . . Allpress,[12] however, described the analogous $TiNb_{52}O_{132}$ as having the stacking sequence . . . CDCDCD . . ., with the unit-cell dimensions $a = 65·6$, $b = 3·82$, $c = 20·9$ Å, $\beta = 104·9°$, and electron microscopic observations in our laboratory have confirmed the latter structure for $Nb_{53}O_{132}$ also.

The Gruehn and Norin sequence has now been recurrently observed in the $MgF_2$–$Nb_2O_5$ system, in a crystal containing lamellae of $M_{28}X_{70}$ structure in a matrix of $M_{25}X_{62}$ structure, as shown in Plate 2. This intergrowth structure, with the general formula $Mg_xNb_{53-x}O_{133-3x}F_{3x-1}$ [Figure 4(b)] would have the unit-cell dimensions $a = 63·2$, $b = 3·82$, $c = 21·2$ Å, $\beta = 94·1°$.

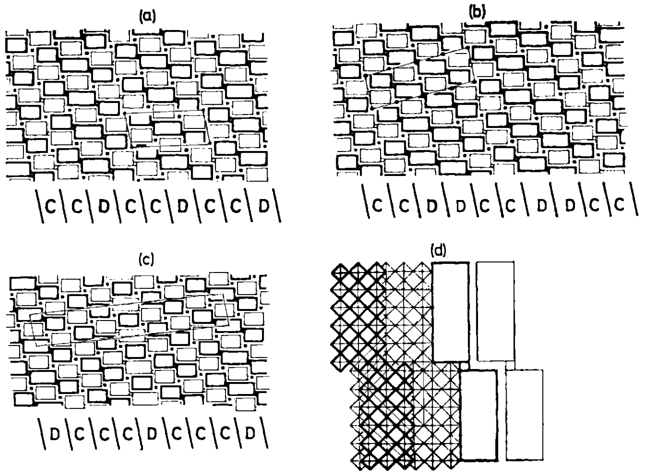

FIGURE 4 (a) Block structures of $M_{39}X_{97}$. (a) $M_{39}X_{973}$, (b) $M_{53}X_{132}$, (c) $M_{103}X_{256}$, and (d) $M_{18}X_{45}$

(iii) $M_{103}X_{256}$. A small domain and several isolated lamellae were also found with the sequence . . . DCCCDCCCD . . . . This ordered array (Plate 1) represents the structure type $M_{103}X_{256}$, a hitherto unreported intergrowth. The unit cell, derived from an idealized model [Figure 4(c)] is $a = 122$, $b = 3·8$, $c = 20·5$ Å, $\beta = 105°$, and the general formula is $Mg_xNb_{103-x}O_{259-3x}F_{3x-3}$; the limiting structure, with [F] = zero, would be $MgNb_{102}O_{256}$; this compound could possibly be prepared from appropriate amounts of MgO and $Nb_2O_5$.

(iv) $M_{18}X_{45}$. ' $M_{18}O_{45}$ ' was described by Wadsley[4] as the hypothetical member, $m = 6$ of the homologous series $M_{3m}O_{8m-3}$. Its existence, however, as yet another block structure modification of $Nb_2O_5$, has not hitherto been reported. In the mixture $MgF_2$–$7Nb_2O_5$ heated at 1000 °C for 1 week we have observed sizeable domains of $(6 \times 3)_\infty$

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[11] K. M. Nimmo and J. S. Anderson, *J.C.S. Dalton*, 1972, 2328.

[12] J. G. Allpress, *J. Solid State Chem.*, 1969, **1**, 66.

[13] R. Gruehn and R. Norin, *Z. anorg. Chem.*, 1967, **355**, 176.

blocks in the configuration corresponding to this structure. In the absence of $MgF_2$, this phase would be $Nb_{18}O_{45}$, a new form of $Nb_2O_5$. In the $MgF_2$–$Nb_2O_5$ system, however, this composition represents the $F^-$-free limit of the general formula $Mg_xNb_{18-x}O_{45-3x}F_{3x}$. Plate 3 shows a domain of this structure coherently intergrown with the (5 × 3) blocks of $M_{15}X_{37}$ structure. The idealized structure is shown in Figure 4(d). It has unit-cell dimensions (based on the model) $a = 20{\cdot}5$, $b = 3{\cdot}82$, $c = 23{\cdot}4$ Å, $\beta = 105°$. These values correspond closely to those predicted by Wadsley for this structure.

## DISCUSSION

*Solubility of* $MgF_2$ *in* $Nb_2O_5$.—The wide range of solubility of $MgF_2$ in $Nb_2O_5$-based block structures was clearly demonstrated in this study. The behaviour of $MgF_2$ as a pseudo-rutile in the system is best illustrated in Table 5, which shows the various known (Ti,Nb) oxides (including those identified electron microscopically by Allpress) and the analogous $MgF_2$,$Nb_2O_5$ composite oxide types found. To emphasize the analogy, the simple compounds lying on the pseudo-binary tie line are listed.

*Comparison of* $MgF_2$*–Niobium oxides,* Ti,Nb *Oxides, and Mixed Valency Binary Niobium Oxides.*—It is of interest to compare the structures found in the binary, ternary, and four-component systems, in particular the capacity for generating intergrowth phases, since three of the basic types of block structure are found in each system. Ordered intergrowths between the $M_{25}X_{62}$ and $M_{12}X_{29}$ structures are found in the $TiO_2$–$Nb_2O_5$ system alone. Extensive electron microscope examination of annealed samples in the binary system revealed no evidence for the formation of the analogous phases $Nb_{37}O_{91}$ or $Nb_{49}O_{120}$, nor for the existence of $Nb_3O_7$.

TABLE 5

Comparison of $TiO_2$–$Nb_2O_5$ and $MgF_2$–$Nb_2O_5$ systems

| Anion : cation ratio | Ti,Nb oxide | Idealized $MgF_2$–$Nb_2O_5$ analogue | Mole % $TiO_2$ : $MgF_2$ |
|---|---|---|---|
| 2·4906 | $TiNb_{52}O_{132}$ | $MgNb_{52}O_{130}F_2$ | 3·7 |
| 2·4872 | $TiNb_{38}O_{97}$ | $MgNb_{38}O_{95}F_2$ | 5·0 |
| 2·4854 | | $Mg_3Nb_{100}O_{250}F_6$ | 6·0 |
| 2·4800 | $TiNb_{24}O_{62}$ | $MgNb_{24}O_{60}F_2$ | 7·7 |
| 2·4667 | | $MgNb_{14}O_{35}F_2$ | 14·3 |
| 2·4595 | $Ti_3Nb_{34}O_{91}$ | | 15 |
| 2·4490 | $Ti_5Nb_{44}O_{120}$ | | 18·5 |
| 2·4167 | $Ti_2Nb_{10}O_{29}$ | $Mg_2Nb_{10}O_{25}F_4$ | 28·5 |
| 2·3333 | $TiNb_2O_7$ | | 50 |

The same three structures are missing from $MgF_2$–$Nb_2O_5$ system. Intergrowths between the H-$Nb_2O_5$ and $M_{25}X_{62}$ structures are common to all structures, and the present system extends these to a **1 : 3** intergrowth, with a very long unit cell. It is noteworthy, moreover, that the **1 : 1** intergrowth in this system has been observed with the structure postulated earlier by Gruehn and Norin, a polymorph of that found in the binary and ternary oxides.

We thank the S.R.C. for support.

[3/877 *Received, 25th April,* 1973]