

# The Crystal Structure of $\text{MgNb}_{14}\text{O}_{35}\text{F}_2$

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A phase analysis of the system  $\text{MgF}_2\text{-Nb}_2\text{O}_5$  has revealed the existence of the compound  $\text{MgNb}_{14}\text{O}_{35}\text{F}_2$ . The crystal structure has been solved from three-dimensional Weissenberg data and refined by least-squares technique. The symmetry is monoclinic, space group  $C2/m$  and the unit cell dimensions:  $a = 20.628 \text{ \AA}$ ;  $b = 3.825 \text{ \AA}$ ;  $c = 19.098 \text{ \AA}$  and  $\beta = 107.75^\circ$ . The structure contains metal-oxygen (fluorine) octahedra which are linked by corners to form blocks measuring  $5 \times 3 \times \infty$  octahedra. The blocks are mutually connected along planes of crystallographic shear by octahedra sharing edges. The structure represents the previously missing member  $n = 5$  of a series of monoclinic block structures  $\text{Me}_{3n}\text{X}_{8n-3}$  found in the  $\text{TiO}_2\text{-Nb}_2\text{O}_5$  system by Wadsley.

## Introduction

The phase equilibrium relations and the crystal structures of the phases in the system  $\text{TiO}_2\text{-Nb}_2\text{O}_5$  have been studied by Wadsley (1), (2), (3) and Roth (3). They found no large solubility of  $\text{TiO}_2$  in  $\text{Nb}_2\text{O}_5$ .

A phase analysis of the system  $\text{MgF}_2\text{-}m\text{Nb}_2\text{O}_5$  was, therefore, started to examine whether the conditions are the same in this system. The result of the phase analysis showed the existence of a phase with a composition corresponding to an  $m$  value of about 7. The Guinier X-ray powder pattern showed great resemblance to those of two substances,  $\text{TiNb}_2\text{O}_7$  and  $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ , belonging to a homologous series of shear structures,  $\text{Me}_{3n}\text{X}_{8n-3}$ , reported by Wadsley (1), (2). An X-ray crystallographic investigation was now started to find the structure and to establish the chemical character of the new compound.

## Experimental

Crystals of the new compound were prepared by mixing of  $\text{MgF}_2$  (Merck's reagent, pro analysi) and  $\text{H-Nb}_2\text{O}_5$  (Kawecki, 99.99%) in a 1:7 ratio. The sample was heated in a sealed platinum tube at  $1000^\circ\text{C}$  for two days. The material thus obtained consisted of rod-shaped, colourless crystals.

The unit cell dimensions determined from a Guinier X-ray powder pattern ( $\text{CuK}\alpha_1$  radiation) were:  $a = 20.628 \text{ \AA} \pm 10$ ;  $b = 3.825 \text{ \AA} \pm 2$ ;  $c = 19.098$

$\text{ \AA} \pm 10$ , and  $\beta = 107.75^\circ \pm 2$ . The indexing of the powder photograph is listed in Table I.

The observed density measured by the apparent loss of weight in benzene is  $4.41 \text{ g cm}^{-3}$ . With two units of  $\text{MgF}_2\text{-}m\text{Nb}_2\text{O}_5$  per elementary cell this would correspond to a value of  $m = 6.94$ . The density value calculated for the stoichiometric formula  $\text{MgNb}_{14}\text{O}_{35}\text{F}_2$ , thus derived for the phase, is  $4.45 \text{ g cm}^{-3}$ .

No real single crystal could be found. Thus, the intensity data were collected from a very small twin with a Weissenberg camera using filtered  $\text{CuK}\alpha$  radiation. The  $h0l$ ,  $h1l$  and  $h2l$  reflexions were recorded by multiple film technique. After separation of the two interpenetrating reciprocal lattices only the reflexions from one of the crystals were visually estimated by means of a standard scale. The  $00l$  reflexions from the twin-individuals overlapped exactly. The contributions from these were determined by measurement of several equivalent non-coincident reflexions.

## Structure Determination

The Weissenberg photographs showed monoclinic symmetry with systematic absences  $hkl$  when  $h + k \neq 2n$ . This condition gave the space group alternatives  $C2$ ,  $Cm$ , and  $C2/m$ . The distribution of  $h0l$  and  $h2l$  intensities with due regard for observational errors and for the effects of thermal motion seemed to be identical. All the atoms were, therefore,

TABLE I  
THE GUINIER POWDER PATTERN OF  
MgNb<sub>14</sub>O<sub>35</sub>F<sub>2</sub> (CuK $\alpha_1$  RADIATION)

<i>I</i>	sin <sup>2</sup> $\theta_{\text{obs}}$	<i>h k l</i>	sin <sup>2</sup> $\theta_{\text{calc}}$
w	0.00592	2 0 1	0.00592
vw	0.00618	2 0 0	0.00615
vw	0.00719	0 0 2	0.00717
w	0.01615	0 0 3	0.01614
m	0.02234	4 0 1	0.02234
m	0.02871	0 0 4	0.02869
vst	0.04206	1 1 0	0.04209
m	0.04282	1 1 1	0.04287
st	0.04482	0 0 5	0.04484
st	0.05033	6 0 2	0.05036
w	0.05116	6 0 1	0.05106
m	0.05308	3 1 1	0.05314
m	0.05566	3 1 2	0.05548
vw	0.06118	2 0 5	0.06111
w	0.07481	1 1 4	0.07483
st	0.07563	5 1 1	0.07571
w	0.07894	5 1 0	0.07898
vw	0.07952	3 1 3	0.07964
w	0.08339	6 0 6	0.08345
w	0.08922	8 0 2	0.08935
w	0.09040	8 0 3	0.09022
w	0.09531	3 1 4	0.09523
w	0.10844	6 0 4	0.10833
m	0.11063	7 1 1	0.11057
st	0.13884	8 0 3	0.13882

assumed to be situated in planes perpendicular to the *y* axis, a distance of *b*/2 apart. The higher symmetry, *C2/m*, was tentatively assumed for the structure investigation. The length of the *b* axis, 3.83 Å, suggested the structure to be built up of layers of polyhedra linked by sharing corners and edges.

The appearance of the Weissenberg photographs gave further support to the idea of a structural relationship existing between the investigated compound and the ternary titanium–niobium oxides in the homologous series Me<sub>3n</sub>X<sub>8n-3</sub> reported by Wadsley (1), (2). The latter structures may be described in terms of blocks consisting of MeX<sub>6</sub> octahedra linked by corners as in the ReO<sub>3</sub> type. The blocks are of finite extension in two dimensions, measuring 3 × 3 and 3 × 4 octahedra and infinite in the third dimension. The blocks are joined by octahedra sharing edges in a complicated way (v. inf.).

The symmetry of TiNb<sub>2</sub>O<sub>7</sub> and Ti<sub>2</sub>Nb<sub>10</sub>O<sub>29</sub> was given by Wadsley as *A2/m*. The space group of MgNb<sub>14</sub>O<sub>35</sub>F<sub>2</sub> is the same but the discussion of this compound will be in terms of the *C*-centered

setting used in the International Tables of Crystallography. The *c* and *b* axes of the two titanium–niobium oxides are very nearly the same which reflects the common finite extension of three MeX<sub>6</sub> octahedra of the building blocks of these substances. The corresponding figures for the *a* and *b* axes of MgNb<sub>14</sub>O<sub>35</sub>F<sub>2</sub> have rather similar values suggesting blocks of this extension to be present also in this material. The extension in the third dimension of the three phases (*a*sin $\beta$  and *c*sin $\beta$ ) increase regularly in the order 10.31 Å (TiNb<sub>2</sub>O<sub>7</sub>), 14.27 Å (Ti<sub>2</sub>Nb<sub>10</sub>O<sub>29</sub>), and 18.19 Å (MgNb<sub>14</sub>O<sub>35</sub>F<sub>2</sub>), which suggests that the block size of the latter is five octahedra in this direction.

The idea thus arrived at was tested by comparison of the observed unit cell dimensions for MgNb<sub>14</sub>O<sub>35</sub>F<sub>2</sub> with the corresponding data for the hypothetical member *n* = 5 of the monoclinic homologous series Me<sub>3n</sub>X<sub>8n-3</sub>:

	<i>a</i>	<i>b</i>	<i>c</i>	$\beta$
obs	20.628 Å	3.825 Å	19.098 Å	107.75°
calc	20.50 Å	3.80 Å	19.45 Å	108.5°

The point positions used in the space group *C2/m* are the following:

$$\begin{aligned}
 &(0, 0, 0; \frac{1}{2}, \frac{1}{2}, 0)+ \\
 &4(i) \quad m \quad x, 0, z; \bar{x}, 0, \bar{z}, \\
 &2(d) \quad 2/m \quad 0, \frac{1}{2}, \frac{1}{2}, \\
 &2(c) \quad 2/m \quad 0, 0, \frac{1}{2}.
 \end{aligned}$$

All the atoms except two metal and two nonmetal atoms of the hypothetical structure occupy 4(*i*) positions, while the remaining atoms occupy the special positions 2(*c*) and 2(*d*), respectively. The coordinate values for the various atoms were calculated by analogy with the data reported for the titanium–niobium oxides.

The preliminary structure factors calculated under the assumption of random occupancies of the metal as well as the nonmetal atom sites were found to be in acceptable agreement with the observed structure factors. Least-squares techniques were applied to refine the parameter values on the basis of the 216 independent reflexions from the *h0l*, *h1l*, and *h2l* layer lines. Owing to the relatively great number of parameters all temperature factors were fixed at 0.5 Å<sup>2</sup> for the metal atoms and 1.0 Å<sup>2</sup> for the anions, during the first stages of refinement. The *R* value dropped to 10.8%. Finally, individual isotropic temperature factors for the metal atoms were included in the refinement. The *R* factor obtained was 6.4%. The atomic parameters are given in Table II. The observed and calculated structure factors are listed in Table III.

TABLE II  
 ATOMIC PARAMETERS IN  $\text{MgNb}_{14}\text{O}_{35}\text{F}_2$ —SPACE GROUP  $C2/m$

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	$\sigma B$
Me(I)	4( <i>i</i> )	0.0630	0	0.0787	0.91	0.35
Me(II)	4( <i>i</i> )	0.1935	$\frac{1}{2}$	0.0791	2.61	0.44
Me(III)	4( <i>i</i> )	0.3736	$\frac{1}{2}$	0.0718	0.62	0.40
Me(IV)	4( <i>i</i> )	0.1208	0	0.2893	0.94	0.41
Me(V)	4( <i>i</i> )	0.2515	$\frac{1}{2}$	0.2838	-0.29	0.33
Me(VI)	4( <i>i</i> )	0.4413	$\frac{1}{2}$	0.2971	0.10	0.42
Me(VII)	4( <i>i</i> )	0.1841	0	0.4991	0.20	0.51
Me(VIII)	2( <i>c</i> )	0	0	$\frac{1}{2}$	1.47	1.08
X(I)	4( <i>i</i> )	0.0857	$\frac{1}{2}$	0.0625		
X(II)	4( <i>i</i> )	0.1565	0	0.0429		
X(III)	4( <i>i</i> )	0.2700	$\frac{1}{2}$	0.0681		
X(IV)	4( <i>i</i> )	0.0878	0	0.1926		
X(V)	4( <i>i</i> )	0.2252	$\frac{1}{2}$	0.1873		
X(VI)	4( <i>i</i> )	0.4105	$\frac{1}{2}$	0.1665		
X(VII)	4( <i>i</i> )	0.1428	$\frac{1}{2}$	0.2790		
X(VIII)	4( <i>i</i> )	0.3413	$\frac{1}{2}$	0.2788		
X(IX)	4( <i>i</i> )	0.4271	0	0.2664		
X(X)	4( <i>i</i> )	0.1588	0	0.3895		
X(XI)	4( <i>i</i> )	0.2904	$\frac{1}{2}$	0.3924		
X(XII)	4( <i>i</i> )	0.2261	0	0.2916		
X(XIII)	4( <i>i</i> )	0.4692	$\frac{1}{2}$	0.0482		
X(XIV)	4( <i>i</i> )	0.3598	0	0.0470		
X(XV)	4( <i>i</i> )	0.0896	0	0.5068		
X(XVI)	4( <i>i</i> )	0.4647	$\frac{1}{2}$	0.3897		
X(XVII)	4( <i>i</i> )	0.0321	0	0.2829		
X(XVIII)	4( <i>i</i> )	0.2046	$\frac{1}{2}$	0.5228		
X(XIX)	2( <i>d</i> )	0	$\frac{1}{2}$	$\frac{1}{2}$		

### Discussion

The structure determination fully confirms the assumption that  $\text{MgNb}_{14}\text{O}_{35}\text{F}_2$  represents the  $n = 5$  member of the monoclinic homologous series  $\text{Me}_{3n}\text{X}_{8n-3}$ . Thus, the structure consists of blocks of  $\text{ReO}_3$  type which extend in the *ac* plane over  $5 \times 3$  octahedra and are of infinite length along the *b* axis. The structural principles for the series  $\text{Me}_{3n}\text{X}_{8n-3}$  are demonstrated by idealized drawings of the three compounds  $\text{TiNb}_2\text{O}_7$ ,  $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ , and  $\text{MgNb}_{14}\text{O}_{35}\text{F}_2$  in Fig. 1.

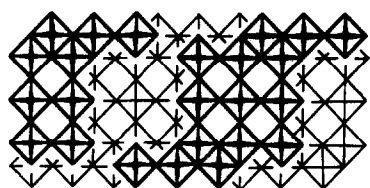
The distortions of the octahedra are shown in Fig. 2 and the metal-anion distances are given in Table IV. In spite of a wide variation among the metal-anion distances the average value, 2.00 Å, is very similar to the distances found in  $\text{H-Nb}_2\text{O}_5$ , 1.99 Å (4), in  $\text{N-Nb}_2\text{O}_5$ , 2.01 Å, (5), and in  $\text{Nb}_3\text{O}_7\text{F}$ , 1.97 Å, (6). The anion-anion distances within the octahedra vary between 2.36–3.30 Å ( $\sigma$  around 0.15 Å). The shortest distances occur for shared edges, as was also observed in  $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$  (2).

The accuracy of the atomic positional parameters and hence also of the interatomic distances is moderate which is obviously due partly to the fact that, because of the twinning an absorption correction could not be made and partly to the number of observed data being low in relation to the number of parameters to be determined. The effect of these shortcomings of the primary material is, however, more likely to be found in the "thermal parameters." As mentioned above the structure refinement had to be carried out with a common fixed value of the *B* parameter of the anions. The values obtained for the metal atoms vary considerably but the e.s.d.'s are also rather high. An interpretation of these values in terms of thermal motion seems unsound. This applies also to calculations of preferred occupancy of the various sites by the two metal atom species. This appreciation of the nonphysical significance of the *B*-parameter values is supported by some exploratory calculations.

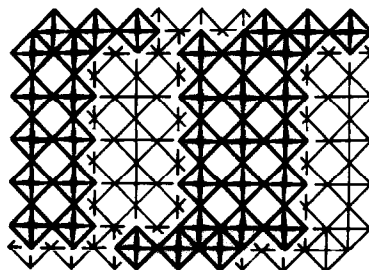
It is interesting to compare the present structure

TABLE III  
OBSERVED AND CALCULATED STRUCTURE FACTORS FOR  $MgNb_{14}O_{35}F_2$

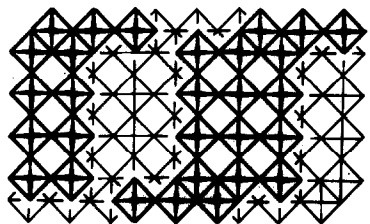
H	K	L	F <sub>O</sub>	F <sub>C</sub>	H	K	L	F <sub>O</sub>	F <sub>C</sub>	H	K	L	F <sub>O</sub>	F <sub>C</sub>	H	K	L	F <sub>O</sub>	F <sub>C</sub>
0	C	2	81	50	8	0	3	126	130	3	1	8	123	-139	0	2	9	590	-605
C	0	3	178	172	8	0	7	227	252	3	1	9	202	199	0	2	10	403	381
0	0	4	429	-390	10	0	-22	214	203	5	1	-11	617	-613	0	2	11	104	83
0	0	5	911	-857	10	0	-17	316	-312	5	1	-7	164	-146	0	2	13	82	72
0	0	6	225	-218	10	0	-13	198	-181	5	1	-6	382	375	0	2	14	469	467
C	C	7	199	-198	10	0	-12	476	468	5	1	-5	150	155	4	2	-6	184	175
0	0	8	269	-262	10	0	-11	137	140	5	1	-4	95	106	4	2	-1	186	-246
0	0	9	836	-795	10	0	-10	103	124	5	1	-3	152	145	6	2	-11	613	-529
C	C	10	472	464	10	0	-9	125	120	5	1	-2	337	388	6	2	-10	145	-129
0	0	11	103	106	10	0	-8	429	464	5	1	-1	524	-473	6	2	-7	360	-308
C	0	13	117	90	10	0	-7	251	-259	5	1	0	161	-155	6	2	-6	355	338
0	0	14	525	546	10	0	-6	132	-147	5	1	1	111	-113	6	2	-5	151	157
2	C	-1	112	100	10	0	-4	90	-88	5	1	2	147	-150	6	2	-4	98	94
2	C	C	64	-82	10	0	0	75	-84	5	1	3	371	-338	6	2	-3	110	110
2	0	4	101	-109	10	0	1	164	-179	5	1	4	179	187	6	2	-2	627	617
2	0	9	156	162	10	0	2	564	553	5	1	8	591	636	6	2	-1	185	-199
4	0	-11	132	-132	10	0	3	101	104	5	1	13	382	-396	6	2	3	477	-475
4	C	-1C	81	86	10	0	4	86	85	7	1	-7	96	-103	6	2	7	122	-168
4	0	-6	-230	206	10	0	5	168	183	7	1	-2	158	173	6	2	8	414	447
4	0	-2	69	62	10	0	6	406	433	7	1	3	111	-95	6	2	12	169	203
4	0	-1	390	-345	10	0	7	331	-333	11	1	-13	613	-548	6	2	13	178	-200
4	0	0	70	-61	10	0	11	382	-359	11	1	-12	322	268	8	2	-12	193	-198
4	C	1	65	-64	10	0	16	306	312	11	1	-11	169	160	8	2	-7	188	175
4	C	2	104	-108	12	0	6	278	280	11	1	-8	715	646	8	2	-3	120	117
4	0	3	163	-164	14	0	-4	131	-137	11	1	-4	201	196	8	2	-2	212	-208
4	0	4	137	135	14	0	1	120	109	11	1	-3	753	-806	10	2	-17	271	-271
4	C	8	261	257	16	0	-14	520	496	11	1	-2	128	-170	10	2	-13	147	-160
6	0	-21	274	-278	16	0	-10	272	274	11	1	-1	106	-101	10	2	-12	404	379
6	0	-20	151	161	16	0	-9	386	-360	11	1	0	132	-143	10	2	-11	105	107
6	0	-16	334	414	16	0	-5	599	-518	11	1	1	409	-405	10	2	-9	95	101
6	0	-11	597	-643	16	0	-4	247	243	11	1	2	415	405	10	2	-8	373	382
6	0	-10	147	-155	16	0	0	508	464	11	1	3	117	127	10	2	-7	220	-206
6	0	-7	369	-351	16	0	5	495	-465	11	1	5	125	142	10	2	-3	599	-635
6	0	-6	404	379	16	0	10	243	240	11	1	6	677	645	10	2	6	372	353
6	0	-5	181	176	22	0	-16	363	422	11	1	7	163	-181	10	2	7	275	-282
6	0	-4	142	141	22	0	-12	112	122	11	1	11	433	-433	10	2	11	378	-315
6	0	-3	153	158	22	0	-11	371	-448	17	1	-14	287	297	12	2	-13	326	-309
6	0	-2	829	810	22	0	-7	293	-290	17	1	-13	191	187	12	2	-8	287	261
6	0	-1	273	-255	22	0	-6	365	351	17	1	-10	341	321	12	2	-4	275	232
6	C	0	122	-114	22	0	-2	413	350	17	1	-9	145	-125	12	2	-3	189	-217
6	0	3	557	-535	22	0	3	373	-392	17	1	0	305	360	16	2	-14	446	433
6	0	6	79	-72	1	1	-5	529	-453	17	1	4	280	244	16	2	-10	256	244
6	0	7	213	-197	1	1	-2	88	-104	17	1	5	283	-252	16	2	-9	299	-317
6	0	8	485	543	1	1	2	133	136	21	1	-11	336	-350	16	2	-8	117	-113
6	0	9	111	109	1	1	3	149	146	21	1	-6	446	418	16	2	-5	478	-445
6	0	10	107	97	1	1	4	293	302	21	1	-1	261	-268	16	2	-4	235	212
6	0	12	244	227	1	1	5	223	-235	21	1	3	345	-355	16	2	0	388	409
6	0	13	239	-227	1	1	8	98	-106	0	2	2	43	50	16	2	5	421	-407
8	0	-12	241	-248	1	1	9	438	-474	0	2	3	109	125	16	2	9	187	-181
8	0	-7	207	211	1	1	14	258	267	0	2	4	280	282	16	2	10	208	216
8	0	-3	158	147	3	1	-6	137	-130	0	2	5	655	-670	22	2	-11	336	-364
8	0	-2	251	-274	3	1	-5	132	124	0	2	6	159	-152	22	2	-7	269	-261
8	0	0	69	-57	3	1	-1	347	320	0	2	7	135	-131	22	2	-6	335	312
8	0	2	148	-145	3	1	4	209	-198	0	2	8	212	-199	22	2	-2	341	313



$TiNb_2O_7$



$MgNb_{14}O_{35}F_2$



$Ti_2Nb_{10}O_{29}$

FIG. 1. Idealized drawings of the structures  $TiNb_2O_7$ ,  $Ti_2Nb_{10}O_{29}$  and  $MgNb_{14}O_{35}F_2$ .

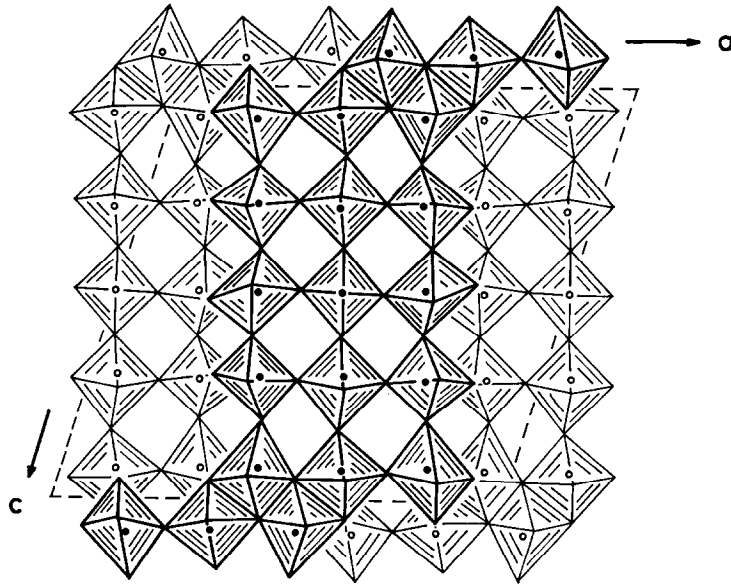


FIG. 2. The crystal structure of  $\text{MgNb}_{14}\text{O}_{35}\text{F}_2$  viewed along the  $b$  axis. ○ Metal atoms at  $y = 0$ ; ● metal atoms at  $y = \frac{1}{2}$ .

TABLE IV

INTERATOMIC DISTANCES IN  $\text{MgNb}_{14}\text{O}_{35}\text{F}_2$ —  
STANDARD DEVIATIONS  $\pm 0.15$  Å

Distance	Å	Mean value
Me(I)–2X(I)	2.01	
X(II)	2.23	
X(IV)	2.08	2.08
X'(XIII)	1.84	
X"(XIII)	2.31	
Me(II)–X(I)	2.15	
2X(II)	2.10	
X(III)	1.65	2.05
X(V)	1.97	
X(XIV)	2.32	
Me(III)–X(II)	2.09	
X(III)	2.12	
X(VI)	1.74	2.01
X(XIII)	2.15	
2X(XIV)	1.97	
Me(IV)–X(IV)	1.76	
2X(VII)	1.99	
X(X)	1.83	1.92
X(XII)	2.16	
X(XVII)	1.80	
Me(V)–X(V)	1.76	
X(VII)	2.22	
X(VIII)	1.88	1.97
X(XI)	1.98	
2X(XII)	2.00	
Me(VI)–X(VI)	2.38	
X(VIII)	1.98	

TABLE IV (continued)

INTERATOMIC DISTANCES IN  $\text{MgNb}_{14}\text{O}_{35}\text{F}_2$ —  
STANDARD DEVIATIONS  $\pm 0.15$  Å

Distance	Å	Mean value
2X(IX)	2.00	2.00
X(XVI)	1.69	
X(XVII)	1.94	
Me(VII)–X(X)	2.00	
X(XI)	1.98	
X(XV)	2.00	2.07
2X'(XVIII)	1.98	
X"(XVIII)	2.45	
Me(VIII)–2X(XV)	1.82	
2X(XVI)	2.01	1.91
2X(XIX)	1.91	

with that of  $\text{MoNb}_{15}\text{O}_{40}\text{F}$  recently reported by Galy and Andersson (7). The latter is also a block-type structure containing the same type of units, measuring  $5 \times 3 \times \infty$  octahedra. However, in this compound, the molybdenum atoms are inserted in tetrahedrally coordinated interstices at the junctions of four blocks. Thus, although the major structural units of the two compounds  $\text{MgNb}_{14}\text{O}_{35}\text{F}_2$  and  $\text{MoNb}_{15}\text{O}_{40}\text{F}$  are identical, they join rather differently.

The  $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$  phase (2) and also the analogous binary niobium oxide  $\text{Nb}_{12}\text{O}_{29}$  (8) exist in two

modifications, which bear a very close structural relation to each other. In addition to the monoclinic form described above, an orthorhombic structure exists which differs from the former essentially by the presence of mirror planes parallel to the *ab* plane in the *C*-centered description of the structure. The orthorhombic modifications of  $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$  and  $\text{Nb}_{12}\text{O}_{29}$  may be looked upon as representing the  $n=4$  members of an orthorhombic homologous series  $\text{Me}_{3n}\text{X}_{8n-3}$ , analogous to the monoclinic series discussed in this paper. No orthorhombic modification of  $\text{TiNb}_2\text{O}_7$  ( $n=3$ ) has been observed. Attempts to prepare an orthorhombic version of  $\text{MgNb}_{14}\text{O}_{35}\text{F}_2$  by heat treatment at different temperatures have so far been without success. It is interesting to observe, however, that the twinning always found in the monoclinic crystals occurs on the *ab* plane.

Detailed descriptions of the structural principles involved in this family of shear structures have been given recently (9), (10) and will not be repeated here.

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### References

1. A. D. WADSLEY, *Acta Cryst.* **14**, 660 (1961).
2. A. D. WADSLEY, *Acta Cryst.* **14**, 664 (1961).
3. R. S. ROTH AND A. D. WADSLEY, *Acta Cryst.* **18**, 724 (1965).
4. B. M. GATEHOUSE AND A. D. WADSLEY, *Acta Cryst.* **17**, 1545 (1964).
5. S. ANDERSSON, *Z. Anorg. Allgem. Chem.* **351**, 106 (1967).
6. S. ANDERSSON, *Acta Chem. Scand.* **18**, 2339 (1964).
7. J. GALY AND S. ANDERSSON, *Acta Cryst.* **B24**, 1027 (1968).
8. R. NORIN, *Acta Chem. Scand.* **17**, 1391 (1965).
9. S. ANDERSSON, *Bull. Soc. Chim. France* 1088 (1965).
10. R. S. ROTH AND A. D. WADSLEY, *Acta Cryst.* **19**, 42 (1965).