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The Crystal Structures of $Nb_{31}O_{77}F$ and $Nb_{17}O_{42}F$

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$Nb_{31}O_{77}F$ is monoclinic with $a = 37.54$ Å, $b = 3.832$ Å, $c = 21.18$ Å, $\beta = 91.92°$, space group $C2$, and $Nb_{17}O_{42}F$ also monoclinic with $a = 21.09$ Å, $b = 3.827$ Å, $c = 23.02$ Å, $\beta = 116.22°$, space group $P2$.

$Nb_{31}O_{77}F$ and $Nb_{17}O_{42}F$ form the members with $n = 10$ and 11 of the homologous series $M_{3n+1}X_{8n-2}$. This series was first proposed by Gatehouse and Wadsley and by Roth and Wadsley in their structure determinations of α-Nb_2O_5 and $TiNb_{24}O_{62}$ ($n = 9$ and 8). The $Nb_{17}O_{42}F$ structure contains two different blocks of ReO_3-type, 3×5 and 3×6 octahedra in size. In the $Nb_{31}O_{77}F$ structure the blocks are of the same kind, *viz.* 3×5 octahedra in size. In both structures the blocks are joined by additional edge sharing and with metal atoms in tetrahedral coordination in the same way as in α-Nb_2O_5.

In his investigation of the system NbO_2F—Nb_2O_5 Andersson [1] found two niobium oxide fluorides of low fluorine contents to form at elevated temperatures. The crystallographic symmetry and cell dimensions as determined by Andersson (Table 1) were found to indicate that the compounds are members of the homologous series $M_{3n+1}X_{8n-2}$, with $n=10$ and $n=11$, respectively. It was thus concluded by Andersson that the formulae of the two compounds should be $Nb_{31}O_{77}F$ and $Nb_{17}O_{42}F$. The series $M_{3n+1}X_{8n-2}$ was first proposed by Gatehouse and Wadsley [2] and by Roth and Wadsley [3] in their structure determinations of α-Nb_2O_5 and $TiNb_{24}O_{62}$ ($n = 9$ and 8, resp.). $Nb_{25}O_{62}$ was later on shown by Norin [4] to be isostructural with $TiNb_{24}O_{62}$. In order to confirm the suggestion concerning their belonging to the homologous series mentioned, a determination of the crystal structures of $Nb_{31}O_{77}F$ and $Nb_{17}O_{42}F$ was undertaken and will now be reported.

Table 1. Crystallographic data for $Nb_{31}O_{77}F$ and $Nb_{17}O_{42}F$.

Compound	Symmetry	Possible space groups	Unit cell dimensions in Å			
$Nb_{31}O_{77}F$	Monoclinic	$C2$, Cm or $C2/m$	37.54	3.832	21.18	91.92°
$Nb_{17}O_{42}F$	Monoclinic	$P2$, Pm or $P2/m$	21.09	3.827	23.02	116.22°

STRUCTURE DETERMINATION

Small needle-shaped crystals of $Nb_{31}O_{77}F$ and $Nb_{17}O_{42}F$ were prepared as reported earlier.[1] The *h0l*, *h1l* and *h2l* levels were recorded by the integrating Weissenberg technique using multiple films and Cu*K* radiation. The crystals were about 0.05 mm long and of 0.01 mm average diameter, so that absorption correction was considered unnecessary. Random occupancy of the anion sites was assumed, and because of the small difference in scattering factor between the two non-metals, one F^- was simply treated as if it were one O^{2-}.

Starting from the known structure of α-Nb_2O_5 ($n = 9$)[2] and assuming $Nb_{17}O_{42}F$ to be the member with $n = 11$ and to have the same space group, $P2$, as α-Nb_2O_5,[1] tentative atomic coordinates of the oxide fluoride phase were deduced. Structure factor calculations with these coordinates gave a very good overall agreement, indicating the assumed structure to be the correct one. The *h0l* and *h1l* structure factors were now used in several least-squares cycles using the Åsbrink-Brändén program written for the computer FACIT. This was made possible by successively keeping parts of the great number of parameters constant. The reliability index R was ultimately reduced to 12.2 % (*h0l*) and 13.5 % (*h1l*). The parameters obtained are given in Table 2, and the comparison between F_o and F_c, which includes an isotropic B of 0.5 for Nb and 1.0 for O, is given in Table 3. The interatomic distances in $Nb_{17}O_{42}F$ are given in Table 4.

Members of the series $M_{3n+1}X_{8n-2}$ with n even belong to the space group $C2$. This is in agreement with what was observed from single crystal data for $Nb_{31}O_{77}F$. Using the structure of $TiNb_{24}O_{62}$ ($n = 8$) and assuming $Nb_{31}O_{77}F$ to be the member $n = 10$, coordinates could thus be obtained. During the refinement of $Nb_{17}O_{42}F$ it was observed that the original coordinates derived from the structure of Nb_2O_5 changed very little. Weighing the probable structural improvement obtained from a refinement of $Nb_{31}O_{77}F$ against the large amount of time required for such an undertaking, this was considered not to be worth while, and in this paper there will only be given a comparison between I_o and I_c of the Guinier X-ray powder pattern (Table 5). The coordinates used are given in Table 6. The structures are illustrated with a ball- and spoke drawing in Fig. 1.

The compounds $Nb_{31}O_{77}F$ and $Nb_{17}O_{42}F$ can also be described as members of the general series $M_{nmp+1}X_{3nmp-(n+m)p+4}$, which was derived for α-Nb_2O_5 and several related structures by Roth and Wadsley.[5] Thus, for $Nb_{31}O_{77}F$ the values of the variables are $n = 3$, $m = 5$, $p = 2$, and for $Nb_{17}O_{42}F$ the corresponding figures are $n = 3$, $m = 5$, $p = 1$ plus $n = 3$, $m = 6$, $p = \infty$.

The structures of $Nb_{31}O_{77}F$ and $Nb_{17}O_{42}F$ can easily be represented by the symbols designed by Andersson[6] for compounds of this kind, which is shown in Fig. 2.

Table 2. Fractional atomic parameters for $Nb_{17}O_{42}F$. Space group $P2$. The average standard deviations for the metal atoms are $\sigma(x) = 0.0021$ and $\sigma(z) = 0.0019$.

Atom	Point position	x	y	z
Nb(1)	1(*a*)	0	0.25	0
Nb(2)	1(*b*)	0	0.5	0.5
Nb(3)	2(*e*)	0.0882	0.5	0.1690
Nb(4)	2(*e*)	0.1385	0.5	0.3482
Nb(5)	2(*e*)	0.1644	0	0.9984
Nb(6)	2(*e*)	0.2232	0	0.1867
Nb(7)	2(*e*)	0.2756	0	0.3708
Nb(8)	2(*e*)	0.3584	0	0.0355
Nb(9)	2(*e*)	0.4225	0	0.2289
Nb(10)	2(*e*)	0.4776	0	0.4149
Nb(11)	2(*e*)	0.5546	0	0.0739
Nb(12)	2(*e*)	0.6151	0	0.2706
Nb(13)	2(*e*)	0.6727	0	0.4458
Nb(14)	2(*e*)	0.6944	0.5	0.0988
Nb(15)	2(*e*)	0.7484	0.5	0.2849
Nb(16)	2(*e*)	0.8024	0.5	0.4646
Nb(17)	2(*e*)	0.8925	0.5	0.1377
Nb(18)	2(*e*)	0.9394	0.5	0.3148
O(1)	1(*b*)	0	0	0.5
O(2)	1(*d*)	0.5	0	0.5
O(3)	2(*e*)	0.045	0.5	0.336
O(4)	2(*e*)	0.049	0.5	0.065
O(5)	2(*e*)	0.116	0.5	0.249
O(6)	2(*e*)	0.158	0.5	0.443
O(7)	2(*e*)	0.108	0	0.166
O(8)	2(*e*)	0.166	0	0.352
O(9)	2(*e*)	0.186	0.5	0.164
O(10)	2(*e*)	0.239	0.5	0.361
O(11)	2(*e*)	0.192	0	0.090
O(12)	2(*e*)	0.237	0	0.276
O(13)	2(*e*)	0.298	0	0.471
O(14)	2(*e*)	0.264	0	0.021
O(15)	2(*e*)	0.319	0	0.204
O(16)	2(*e*)	0.372	0	0.382
O(17)	2(*e*)	0.348	0.5	0.012
O(18)	2(*e*)	0.392	0	0.124
O(19)	2(*e*)	0.422	0.5	0.229
O(20)	2(*e*)	0.450	0	0.317
O(21)	2(*e*)	0.479	0.5	0.415
O(22)	2(*e*)	0.456	0	0.025
O(23)	2(*e*)	0.517	0	0.234
O(24)	2(*e*)	0.562	0	0.430
O(25)	2(*e*)	0.572	0	0.155
O(26)	2(*e*)	0.635	0	0.352
O(27)	2(*e*)	0.600	0.5	0.086
O(28)	2(*e*)	0.633	0.5	0.250
O(29)	2(*e*)	0.702	0.5	0.443
O(30)	2(*e*)	0.664	0	0.074
O)31)	2(*e*)	0.720	0.5	0.208
O(32)	2(*e*)	0.719	0	0.275
O(33)	2(*e*)	0.783	0.5	0.385
O(34)	2(*e*)	0.779	0	0.462

Atom	Point position	x	y	z
O(35)	2(*e*)	0.792	0.5	0.104
O(36)	2(*e*)	0.833	0.5	0.296
O(37)	2(*e*)	0.887	0.5	0.473
O(38)	2(*e*)	0.846	0.5	0.026
O(39)	2(*e*)	0.875	0	0.104
O(40)	2(*e*)	0.915	0.5	0.217
O(41)	2(*e*)	0.938	0	0.320
O(42)	2(*e*)	0.973	0.5	0.425
O(43)	2(*e*)	0.946	0	0.025
O(44)	2(*e*)	0.971	0.5	0.130

Table 3. Comparison of observed and calculated structure factors for $Nb_{17}O_{42}F$.

$h\ k\ l$	F_o	F_c	$h\ k\ l$	F_o	F_c
0 0 2	57	93	5 0 $\bar{15}$	249	195
0 0 6	90	91	6 0 $\bar{13}$	162	166
0 0 11	205	222	6 0 $\bar{12}$	154	170
0 0 $\bar{22}$	187	235	6 0 $\bar{6}$	93	81
1 0 $\bar{12}$	122	102	6 0 $\bar{5}$	112	122
1 0 $\bar{9}$	139	137	6 0 $\bar{4}$	133	149
1 0 $\bar{8}$	132	115	6 0 $\bar{3}$	194	206
1 0 $\bar{7}$	202	179	6 0 $\bar{2}$	966	1008
1 0 $\bar{6}$	790	1106	6 0 $\bar{1}$	220	181
1 0 $\bar{5}$	303	396	6 0 9	351	317
1 0 $\bar{4}$	132	168	6 0 $\bar{20}$	439	426
1 0 $\bar{3}$	73	94	7 0 $\bar{11}$	112	119
1 0 3	54	43	7 0 $\bar{9}$	161	175
1 0 5	122	208	7 0 $\bar{8}$	499	548
1 0 $\bar{16}$	292	325	7 0 $\bar{7}$	352	328
2 0 $\bar{12}$	583	656	7 0 $\bar{6}$	116	134
2 0 $\bar{11}$	731	863	7 0 3	231	243
2 0 $\bar{10}$	297	327	7 0 4	98	74
2 0 $\bar{9}$	199	172	7 0 13	144	145
2 0 $\bar{6}$	94	95	7 0 $\bar{14}$	428	495
2 0 $\bar{1}$	132	142	8 0 $\bar{14}$	297	298
2 0 0	97	95	8 0 $\bar{13}$	622	659
2 0 10	293	344	8 0 $\bar{12}$	187	239
2 0 $\bar{21}$	403	311	8 0 $\bar{3}$	222	212
3 0 $\bar{17}$	625	628	8 0 $\bar{2}$	300	242
3 0 $\bar{16}$	184	143	8 0 7	171	193
3 0 4	161	223	8 0 8	579	522
3 0 5	174	274	8 0 $\bar{9}$	374	421
3 0 13	183	139	9 0 $\bar{19}$	481	529
3 0 15	345	240	9 0 $\bar{8}$	224	215
3 0 $\bar{16}$	300	274	9 0 2	275	261
4 0 $\bar{23}$	584	507	9 0 3	609	676
4 0 $\bar{2}$	118	138	9 0 $\bar{4}$	112	74
4 0 $\bar{1}$	367	439	10 0 $\bar{25}$	364	383
4 0 0	94	46	10 0 $\bar{14}$	265	220
4 0 8	145	152	10 0 $\bar{3}$	960	969
4 0 9	315	250	10 0 $\bar{8}$	316	244
4 0 10	544	577	11 0 $\bar{9}$	551	540
5 0 $\bar{7}$	239	181	11 0 $\bar{8}$	305	312
5 0 4	618	617	11 0 $\bar{7}$	203	176

$h\,k\,l$	F_o	F_c	$h\,k\,l$	F_o	F_c
11 0 $\bar{6}$	154	144	2 1 $\bar{1}\bar{7}$	352	232
11 0 2	457	291	2 1 $\bar{6}$	448	591
12 0 $\bar{1}\bar{5}$	329	319	2 1 $\bar{5}$	234	207
12 0 $\bar{1}\bar{4}$	560	550	2 1 16	473	499
12 0 $\bar{1}\bar{3}$	229	258	3 1 $\bar{2}\bar{3}$	199	134
12 0 $\bar{1}\bar{2}$	174	154	3 1 $\bar{1}\bar{2}$	536	613
12 0 $\bar{1}\bar{1}$	118	119	3 1 $\bar{1}$	326	391
12 0 $\bar{9}$	113	121	3 1 10	658	737
12 0 $\bar{7}$	135	153	4 1 $\bar{1}\bar{8}$	355	387
12 0 $\bar{5}$	174	211	4 1 $\bar{7}$	205	222
12 0 $\bar{4}$	475	412	4 1 $\bar{6}$	130	111
12 0 $\bar{3}$	220	111	4 1 2	95	108
13 0 $\bar{2}\bar{0}$	392	397	4 1 3	152	178
13 0 $\bar{1}\bar{0}$	281	226	4 1 4	389	463
13 0 $\bar{9}$	326	227	4 1 5	235	256
13 0 11	178	204	5 1 $\bar{2}\bar{3}$	326	334
13 0 12	277	309	5 1 $\bar{1}\bar{2}$	235	221
14 0 $\bar{2}\bar{6}$	319	309	5 1 $\bar{4}$	126	108
14 0 $\bar{1}\bar{5}$	384	372	5 1 $\bar{3}$	166	163
14 0 6	242	227	5 1 $\bar{2}$	467	543
14 0 7	468	480	5 1 $\bar{1}$	471	556
15 0 $\bar{2}\bar{1}$	268	334	5 1 0	187	172
15 0 1	579	559	5 1 1	88	100
16 0 $\bar{2}\bar{7}$	161	206	6 1 $\bar{8}$	189	205
16 0 $\bar{5}$	676	658	6 1 7	392	427
16 0 $\bar{4}$	194	186	6 1 $\bar{6}$	173	124
17 0 $\bar{2}\bar{7}$	139	136	6 1 $\bar{5}$	110	122
17 0 $\bar{1}\bar{1}$	361	376	7 1 $\bar{1}\bar{3}$	597	675
17 0 $\bar{1}\bar{0}$	342	356	7 1 $\bar{2}$	184	155
17 0 $\bar{9}$	197	136	7 1 19	262	202
18 0 $\bar{1}\bar{7}$	198	211	7 1 20	297	283
18 0 $\bar{1}\bar{6}$	516	537	8 1 $\bar{1}\bar{9}$	457	401
18 0 $\bar{1}\bar{5}$	204	194	8 1 $\bar{8}$	187	197
19 0 $\bar{2}\bar{2}$	387	441	8 1 $\bar{1}\bar{4}$	493	483
22 0 $\bar{7}$	483	420	9 1 $\bar{2}\bar{5}$	221	221
22 0 $\bar{6}$	309	241	9 1 $\bar{2}\bar{4}$	294	272
22 0 $\bar{5}$	167	107	9 1 7	173	176
23 0 $\bar{1}\bar{2}$	383	402	9 1 8	732	744
25 0 $\bar{6}$	116	72	10 1 1	245	226
			10 1 2	534	540
			10 1 3	413	401
0 1 1	84	124	11 1 $\bar{6}$	128	113
0 1 2	110	148	11 1 $\bar{4}$	390	393
0 1 3	144	173	11 1 $\bar{3}$	782	847
0 1 4	196	198	11 1 $\bar{2}$	241	210
0 1 5	336	379	12 1 $\bar{9}$	707	786
0 1 6	229	198	12 1 13	149	266
1 1 $\bar{1}\bar{1}$	553	527	13 1 $\bar{1}\bar{5}$	732	734
1 1 $\bar{1}\bar{0}$	144	147	13 1 $\bar{4}$	219	227
1 1 $\bar{3}$	96	110	13 1 7	261	315
1 1 $\bar{2}$	145	158	14 1 $\bar{2}\bar{1}$	376	397
1 1 $\bar{1}$	238	351	14 1 $\bar{2}\bar{0}$	310	320
1 1 1	93	118	14 1 $\bar{1}\bar{9}$	171	158
1 1 10	177	180	14 1 12	232	226
1 1 11	189	159	15 1 $\bar{2}\bar{7}$	109	159
1 1 20	233	220	15 1 $\bar{2}\bar{6}$	378	433
1 1 21	341	291	15 1 $\bar{2}\bar{5}$	137	156
1 1 22	306	256	15 1 6	336	307

$h\ k\ l$	F_o	F_c	$h\ k\ l$	F_o	F_c
15 1 7	143	142	20 1 $\bar{2}\bar{2}$	287	299
16 1 1	413	281	20 1 $\bar{2}\bar{1}$	144	147
17 1 $\bar{1}\bar{6}$	187	208	20 1 $\bar{1}$	271	323
17 1 $\bar{5}$	609	485	20 1 0	226	286
18 1 $\bar{1}\bar{1}$	567	442	21 1 $\bar{2}\bar{1}$	133	98
18 1 0	238	239	21 1 $\bar{1}\bar{7}$	243	201
19 1 $\bar{1}\bar{7}$	390	354	21 1 $\bar{6}$	481	471
19 1 $\bar{1}\bar{6}$	238	204	22 1 $\bar{1}\bar{2}$	425	449
19 1 $\bar{6}$	259	241	23 1 $\bar{7}$	212	128
19 1 $\bar{5}$	403	445	24 1 $\bar{1}\bar{3}$	220	127
20 1 $\bar{2}\bar{3}$	178	175			

Table 4. Interatomic distances for $Nb_{17}O_{42}F$.

Metal atoms	Bonded oxygen atoms *	Nb—O distances (Å) (same order as in previous col.)	Average	O—O distances (Å) max	min	average
Nb(1)	4, 4′, 43, 43′	1.69, 1.69, 1.77, 1.77	1.73	2.98	2.74	2.76
Nb(2)	1(2); 37, 37′, 42, 42′	1.92(2); 2.33, 2.33, 1.57, 1.57	1.94	3.02	2.48	2.76
Nb(3)	7(2); 4, 9, 5, 44	1.97(2); 2.16, 2.11, 1.67, 2.23	2.02	3.07	2.67	2.81
Nb(4)	8(2); 3, 5, 6, 10	1.92(2); 1.83, 2.11, 2.03, 2.02	2.00	3.06	2.59	2.85
Nb(5)	38′(2); 14, 39′, 43′, 11	1.98(2); 1.92, 2.13, 2.14, 1.93	2.01	3.06	2.65	2.85
Nb(6)	9(2); 7, 15, 11, 12	2.05(2); 2.25, 1.89, 2.01, 1.94	2.03	3.00	2.61	2.83
Nb(7)	10(2); 13, 16, 8, 12	2.04(2); 2.14, 1.93, 2.16, 1.97	2.05	3.07	2.72	2.87
Nb(8)	17(2); 14, 18, 22, 30′	1.98(2); 1.87, 1.85, 2.18, 2.35	2.04	3.17	2.54	2.87
Nb(9)	19(2); 15, 18, 20, 23	1.92(2); 1.99, 2.20, 1.85, 1.94	1.97	2.92	2.66	2.80
Nb(10)	21(2); 2, 16, 20, 24	1.92(2); 1.80, 2.01, 2.06, 1.66	1.90	2.85	2.49	2.69
Nb(11)	27(2); 22, 22′, 25, 30	2.10(2); 1.88, 2.19, 1.74, 2.30	2.05	3.24	2.54	2.84
Nb(12)	28(2); 23, 25, 26, 32	2.04(2); 1.86, 2.40, 1.73, 2.15	2.04	3.11	2.55	2.88
Nb(13)	29(2); 13′, 24, 26, 34	2.02(2); 1.74, 2.19, 2.26, 2.10	2.06	3.17	2.68	2.90
Nb(14)	30(2); 17′, 27, 31, 35	2.02(2); 2.29, 1.89, 2.32, 1.99	2.09	3.37	2.68	3.02
Nb(15)	32(2); 28, 31, 33, 36	2.00(2); 2.21, 1.60, 2.08, 1.68	1.93	3.31	2.33	2.71
Nb(16)	34(2); 6′, 29, 33, 37	1.97(2); 1.92, 1.96, 1.70, 1.70	1.87	2.76	2.30	2.61
Nb(17)	39(2); 35, 38, 40, 44	2.04(2); 1.92, 2.31, 1.67, 1.74	1.95	3.03	2.51	2.72
Nb(18)	41(2); 3, 36, 40, 42	1.92(2); 2.08, 2.10, 2.07, 2.30	2.07	3.13	2.87	2.97

* Given by numbers (Table 2, Fig. 1a). The first, followed by (2) and a semicolon, are the two oxygen atoms lying over and under the metal. E.s.d.'s of metal-oxygen distances are ± 0.10 Å, for oxygen-oxygen ± 0.15 Å.

Table 5. Comparison of observed and calculated intensities for $Nb_{31}O_{77}F$.

$\sin^2\theta_{obs}$	$h\ k\ l$	$\sin^2\theta_{calc}$	I_{obs}	I_{calc}
	0 0 1	0.00133	—	0.4
0.00170	2 0 0	0.00169	5.7	4.6
	$\bar{2}$ 0 1	0.00292	—	1.8
	2 0 1	0.00312	—	0.4
0.00521	0 0 2	0.00530	6.0	4.4
0.00680	$\bar{4}$ 0 0	0.00676	10.6	3.9
	$\bar{2}$ 0 2	0.00679		4.8
	2 0 2	0.00720	—	0
	$\bar{4}$ 0 1	0.00788	—	1.5
	4 0 1	0.00828	—	0.4
	$\bar{4}$ 0 2	0.01166	—	0.6
	0 0 3	0.01194	—	1.6
	4 0 2	0.01246	—	0.1
	$\bar{2}$ 0 3	0.01333	—	1.0
	2 0 3	0.01393	—	1.3
0.01515	6 0 0	0.01520	5.7	6.6
	$\bar{6}$ 0 1	0.01623	—	2.4
0.01681	6 0 1	0.01683	3.8	4.2
	$\bar{4}$ 0 3	0.01809	—	0.8
	4 0 3	0.01929	—	0.4
	$\bar{6}$ 0 2	0.01990	—	0.9
0.02119	6 0 2	0.02111	1.9	0.4
	0 0 4	0.02122		1.0
	6 0 3	0.02623	—	0
0.02247	$\bar{2}$ 0 4	0.02251	36.5	53.0
	2 0 4	0.02331	—	0
	8 0 0	0.02702	—	2.9
	$\bar{4}$ 0 4	0.02717	—	1.1
	$\bar{8}$ 0 1	0.02795	—	2.3
	6 0 3	0.02804	—	1.6
0.02871	8 0 1	0.02875	24.7	19.8
	4 0 4	0.02878	—	0.1
	$\bar{8}$ 0 2	0.03152	—	0.4
	8 0 2	0.03313	—	2.7
	0 0 5	0.03316	—	0.3
	$\bar{2}$ 0 5	0.03435	—	1.2
	$\bar{6}$ 0 4	0.03522	—	2.5
	2 0 5	0.03335	—	1.5
	6 0 4	0.03762	—	0
	$\bar{8}$ 0 3	0.03776	—	0
	$\bar{4}$ 0 5	0.03891	—	0
	8 0 3	0.04016	—	2.6
0.04079	1 1 0	0.04089	11.4	11.6
	4 0 5	0.04092	—	0.1
0.04214	$\bar{1}$ 1 1	0.04217	121.6	102.0
	10 0 0	0.04222		0.2
	1 1 1	0.04227		41.2
	$\bar{10}$ 0 1	0.04305	—	4.4
0.04407	10 0 1	0.04405	157.3	176.0
	3 1 0	0.04427		12.0
0.04560	$\bar{3}$ 1 1	0.04545	7.6	1.1
	3 1 1	0.04575		11.6
	$\bar{1}$ 1 2	0.04610	—	0.6
	1 1 2	0.04630	—	1.0
	$\bar{10}$ 0 2	0.04652	—	0
	$\bar{8}$ 0 4	0.04663	—	0.8

$\sin^2\theta_{obs}$	$h\ k\ l$	$\sin^2\theta_{calc}$	I_{obs}	I_{calc}
	$\bar{6}\ 0\ 5$	0.04685	—	0.6
0.04790	0 0 6	0.04774	13.3	13.3
	10 0 2	0.04852	—	1.5
0.04881	$\bar{2}\ 0\ 6$	0.04883	122.4	131
	$\bar{3}\ 1\ 2$	0.04928	—	0.6
	8 0 4	0.04984	—	0
	6 0 5	0.04987	5.7	6.2
	2 0 6	0.05003	—	1.7
0.05091	5 1 0	0.05103	13.3	12.8
	$\bar{5}\ 1\ 1$	0.05211	—	0.3
0.05249	5 1 1	0.05260	3.8	4.6
	$\bar{10}\ 0\ 3$	0.05265	—	1.4
0.05263	$\bar{1}\ 1\ 3$	0.05268	52.4	46.8
	1 1 3	0.05298	—	2.8
	10 0 3	0.05566	—	0
0.05580	4 0 6	0.05570	3.8	5.3
	$\bar{3}\ 1\ 3$	0.05576	—	0.4
	$\bar{5}\ 1\ 2$	0.05583	—	0.2
	3 1 3	0.0566	—	0.8
	5 1 2	0.05683	—	0.4
	1 1 3	0.05298	—	2.8
	$\bar{4}\ 0\ 6$	0.05329	—	1.6
	$\bar{8}\ 0\ 5$	0.05817	—	0.2
0.06065	12 0 0	0.06079	3.8	4.6
0.06100	6 0 6	0.06114	15.2	0.4
	7 1 0	0.06116		14.6
	$\bar{10}\ 0\ 4$	0.06143	—	2.5
	$\bar{12}\ 0\ 1$	0.06152	—	0
	$\bar{1}\ 1\ 4$	0.06191		0.8
	$\bar{7}\ 1\ 1$	0.06213		0.6
0.06196	8 0 5	0.06218	4.6	2.8
	5 1 3	0.06221		1.0
	1 1 4	0.06231		1.2
	12 0 1	0.06272		3.1
0.06260	7 1 1	0.06284	7.6	2.6
	5 1 3	0.06372		1.8
	6 0 6	0.06475	—	0.8
	$\bar{3}\ 1\ 4$	0.06489	—	0.8
	$\bar{12}\ 0\ 2$	0.06490	—	0
	0 0 7	0.06499	—	0.3
	$\bar{10}\ 0\ 4$	0.06544	—	0.3
	$\bar{7}\ 1\ 2$	0.06576	—	0.2
	$\bar{2}\ 0\ 7$	0.06597	—	0.1
	3 1 4	0.06609	—	0.3
	7 1 2	0.06716	—	1.5
	12 0 2	0.06730	—	0.3
	2 0 7	0.06738	—	0.1
	$\bar{4}\ 0\ 7$	0.07034	—	0.7
0.07103	$\bar{12}\ 0\ 3$	0.07093	7.6	5.7
	$\bar{5}\ 1\ 4$	0.07124		1.4
	$\bar{7}\ 1\ 3$	0.07204	—	0.4
	$\bar{8}\ 0\ 6$	0.07235	—	0.6
	$\bar{10}\ 0\ 5$	0.07287	—	0.7
	4 0 7	0.07314	—	0
	5 1 4	0.07325	—	0.2
0.07369	$\bar{1}\ 1\ 5$	0.07380	45.2	37.0
	7 1 3	0.07415	—	0.4

$\sin^2\theta_{obs}$	$h\ k\ l$	$\sin^2\theta_{calc}$	I_{obs}	I_{calc}
	1 1 5	0.07430		5.3
0.07451	12 0 3	0.07454	43.7	0.2
	$\bar{9}$ 1 0	0.07467		33.3
	$\bar{9}$ 1 1	0.07555	—	1.0
	9 1 1	0.07645		2.3
0.07646	3 1 5	0.07668	52.8	39.0
	8 0 6	0.07717	—	1.4
	10 0 5	0.07788	—	0.4
	$\bar{6}$ 0 7	0.07808	—	0.9
	3 1 5	0.07818	—	1.0
	$\bar{9}$ 1 2	0.07907	—	2.3
	$\bar{12}$ 0 4	0.07960	—	0.8
0.08067	9 1 2	0.08087	44.1	39.5
	$\bar{7}$ 1 4	0.08097	—	1.7
0.08201	6 0 7	0.08229	4.6	3.5
	14 0 0	0.08275		1.3
0.08273	$\bar{5}$ 1 5	0.08293	4.6	2.1
	$\bar{14}$ 0 1	0.08337	—	0.1
	7 1 4	0.08378	—	0.3
	12 0 4	0.08442	—	0
	14 0 1	0.08478	—	1.9
	0 0 8	0.08488	—	0.9
	$\bar{9}$ 1 3	0.08525	—	0.2
	5 1 5	0.08544	—	0.8
0.08551	$\bar{2}$ 0 8	0.08577	3.8	2.3
	$\bar{14}$ 0 2	0.08665	—	0
	$\bar{10}$ 0 6	0.08695	—	0.4
	2 0 8	0.08737	—	0
	9 1 3	0.08796	—	0.8
0.08812	$\bar{1}$ 1 6	0.08834	3.8	3.2
	1 1 6	0.08894	—	1.4
	$\bar{8}$ 0 7	0.08920	—	0.4
	14 0 2	0.08946		1.8
0.08997	4 0 8	0.09003	3.8	2.3
0.09091	$\bar{12}$ 0 5	0.09094	30.4	22.1
	$\bar{3}$ 1 6	0.09111	—	1.2
	$\bar{11}$ 1 0	0.09156	—	3.3
	$\bar{11}$ 1 1	0.09233	—	0.8
	$\bar{7}$ 1 5	0.09256	—	2.4
	$\bar{14}$ 0 3	0.09258	—	2.1
	3 1 6	0.09292		4.5
0.09300	10 0 6	0.09297	5.7	1.1
	4 0 8	0.09324	—	0.2
	11 1 1	0.09343	—	0.6
	$\bar{9}$ 1 4	0.09408		4.8
0.09446	8 0 7	0.09481	22.0	18.4
0.09564	$\bar{11}$ 1 2	0.09575	8.0	6.6
	7 1 5	0.09607	—	0.1
	14 0 3	0.09679	—	0
	12 0 5	0.09696	—	0
0.09700	$\bar{5}$ 1 6	0.09726	1.9	2.3
	$\bar{6}$ 0 8	0.09767	—	0
0.09771	9 1 4	0.09769	7.6	8.2
	11 1 2	0.09796	—	0.1
0.09984	$\bar{5}$ 1 6	0.10028	3.8	3.0
	$\bar{14}$ 0 4	0.10116	—	1.0
	$\bar{11}$ 1 3	0.10184	—	0.5
	6 0 8	0.10249	—	0.1

$\sin^2\theta_{obs}$	$h\ k\ l$	$\sin^2\theta_{calc}$	I_{obs}	I_{calc}
	$\bar{1}\bar{0}\ 0\ 7$	0.10369	—	1.2
	$\bar{1}\bar{2}\ 0\ 6$	0.10493	—	0.3
	$11\ 1\ 3$	0.10515	—	1.2
	$\bar{1}\ 1\ 7$	0.10553	—	0.3
	$\bar{9}\ 1\ 5$	0.10557	—	0.5
	$1\ 1\ 7$	0.10623	—	1.0
	$14\ 0\ 4$	0.10677	—	0.6
	$\bar{7}\ 1\ 6$	0.10679	—	1.1
	$0\ 0\ 9$	0.10743	—	0.2
	$16\ 0\ 0$	0.10808	—	1.3
	$\bar{3}\ 1\ 7$	0.10821	—	1.2
	$\bar{2}\ 9\ 0$	0.10821	—	0.2
	$\bar{1}\bar{6}\ 0\ 1$	0.10860	—	0.1
	$\bar{8}\ 0\ 8$	0.10869	—	0.2
	$2\ 0\ 9$	0.11002	—	0.5
	$9\ 1\ 5$	0.11008	—	0.4
0.11039	$16\ 0\ 1$	0.11021	45.6	1.5
	$3\ 1\ 7$	0.11031		0.3
	$\bar{1}\bar{1}\ 1\ 4$	0.11057		20.1
	$10\ 0\ 7$	0.11071		3.4
	$7\ 1\ 6$	0.11101		20.1
	$\bar{1}\bar{6}\ 0\ 2$	0.11178	—	0
	$13\ 1\ 0$	0.11182	—	0.5
	$12\ 0\ 6$	0.11215	—	1.6
	$\bar{4}\ 0\ 9$	0.11238	—	0.1
	$\bar{1}\bar{4}\ 0\ 5$	0.11239	—	0
	$\bar{1}\bar{3}\ 1\ 1$	0.11249	—	0.1
	$13\ 1\ 1$	0.11380	—	0.8
	$\bar{5}\ 1\ 7$	0.11426	—	0.4
0.11463	$11\ 1\ 4$	0.11498	6.1	1.2
	$16\ 0\ 2$	0.11499		5.1
	$8\ 0\ 8$	0.11511	—	0.2
	$\bar{1}\bar{3}\ 1\ 2$	0.11582	—	0.1
	$4\ 0\ 9$	0.11599	—	0.2
	$16\ 0\ 3$	0.11761	—	0.5
	$5\ 1\ 7$	0.11777	—	0.5
	$13\ 1\ 2$	0.11843	—	0.1
	$14\ 0\ 5$	0.11941	—	0.3
	$\bar{9}\ 1\ 6$	0.11970	—	2.6
	$\bar{6}\ 0\ 9$	0.11992	—	0.8

Table 6. Fractional atomic parameters for $Nb_{31}O_{77}F$. Space group *C*2.

Atom	Point position	*x*	*y*	*z*
Nb(1)	2(*a*)	0	0.25	0
Nb(2)	4(*c*)	0.091	0	0.005
Nb(3)	4(*c*)	0.192	0	0.038
Nb(4)	4(*c*)	0.294	0	0.090
Nb(5)	4(*c*)	0.395	0	0.128
Nb(6)	4(*c*)	0.499	0	0.162
Nb(7)	4(*c*)	0	0.5	0.157
Nb(8)	4(*c*)	0.072	0	0.176
Nb(9)	4(*c*)	0.174	0	0.219
Nb(10)	4(*c*)	0.272	0	0.266
Nb(11)	4(*c*)	0.374	0	0.304
Nb(12)	4(*c*)	0.481	0	0.337
Nb(13)	4(*c*)	0.056	0	0.361
Nb(14)	4(*c*)	0.158	0	0.394
Nb(15)	4(*c*)	0.256	0	0.447
Nb(16)	4(*c*)	0.352	0	0.475
Nb(17)	4(*c*)	0.043	0.5	0.485
O(1)	4(*c*)	0.139	0	0.014
O(2)	4(*c*)	0.200	0.5	0.014
O(3)	4(*c*)	0.243	0	0.057
O(4)	4(*c*)	0.344	0	0.100
O(5)	4(*c*)	0.299	0.5	0.057
O(6)	4(*c*)	0.401	0.5	0.090
O(7)	4(*c*)	0.406	0	0.038
O(8)	4(*c*)	0.462	0.5	0.190
O(9)	4(*c*)	0.446	0	0.138
O(10)	4(*c*)	0.011	0.5	0.071
O(11)	4(*c*)	0.077	0	0.081
O(12)	4(*c*)	0.182	0	0.128
O(13)	4(*c*)	0.283	0	0.176
O(14)	4(*c*)	0.387	0	0.214
O(15)	4(*c*)	0.491	0	0.252
O(16)	4(*c*)	0.013	0	0.166
O(17)	4(*c*)	0.059	0.5	0.181
O(18)	4(*c*)	0.117	0	0.195
O(19)	4(*c*)	0.174	0.5	0.219
O(20)	4(*c*)	0.224	0	0.238
O(21)	4(*c*)	0.275	0.5	0.266
O(22)	4(*c*)	0.328	0	0.280
O(23)	4(*c*)	0.374	0.5	0.304
O(24)	4(*c*)	0.430	0	0.333
O(25)	4(*c*)	0.497	0.5	0.352
O(26)	4(*c*)	0.059	0	0.271
O(27)	4(*c*)	0.166	0	0.314
O(28)	4(*c*)	0.267	0	0.361
O(29)	4(*c*)	0.368	0	0.399
O(30)	4(*c*)	0.486	0	0.442
O(31)	4(*c*)	0.045	0.5	0.380
O(32)	4(*c*)	0.104	0	0.380
O(33)	4(*c*)	0.155	0.5	0.418
O(34)	4(*c*)	0.206	0	0.413
O(35)	4(*c*)	0.251	0.5	0.475
O(36)	4(*c*)	0.307	0	0.461
O(37)	4(*c*)	0.414	0	0.498
O(38)	4(*c*)	0.043	0	0.451
O(39)	4(*c*)	0.147	0	0.494

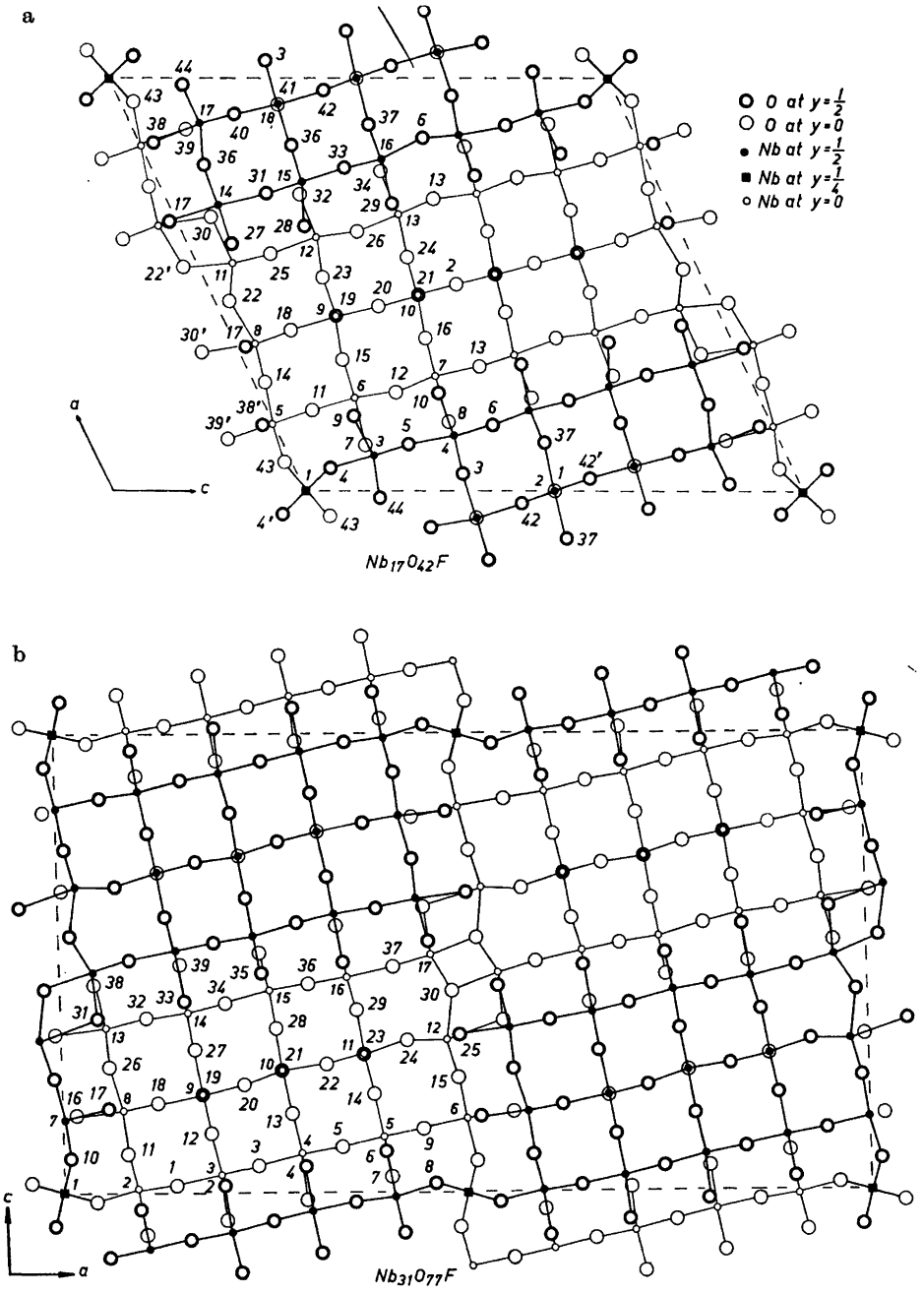


Fig. 1. The structures of $Nb_{17}O_{42}F$ (a) and $Nb_{31}O_{77}F$ (b) projected on (010). Smaller numbers are metal, larger oxygen.

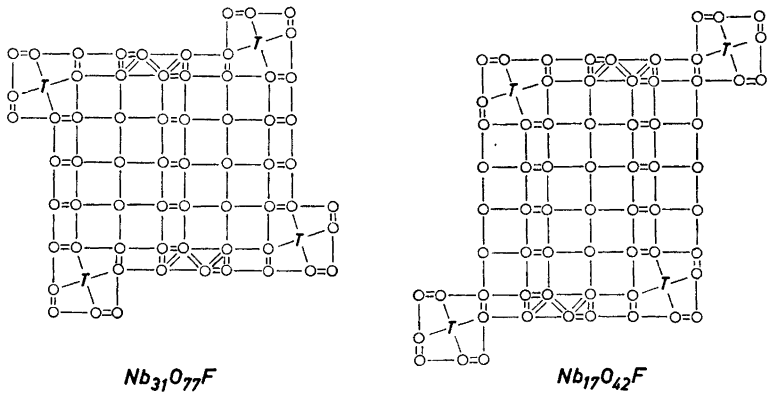
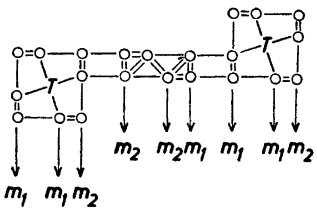


Fig. 2. Symbolic representation of the structures of $Nb_{31}O_{77}F$ and $Nb_{17}O_{42}F$. Circle means octahedron, T means tetrahedron, single line means one oxygen atom shared between two metal atoms, double line means two oxygens shared between two metal atoms (octahedral edge sharing).

The series $M_{3n+1}X_{8n-2}$ can be generally represented by the symbol:



$m_1 + m_2$ is here equal to n in the series $M_{3n+1}X_{8n-2}$.

The structures of the following compounds can thus be obtained by two sets of values of m_1 and m_2:

$TiNb_{24}O_{62}$ ($m_1 = 4$, $m_2 = 4$), Nb_2O_5 ($m_1 = 4$, $m_2 = 5$)
$Nb_{31}O_{77}F$ ($m_1 = 5$, $m_2 = 5$) and $Nb_{17}O_{42}F$ ($m_1 = 5$, $m_2 = 6$)

When m_1 and m_2 grow infinite the structure will be the parent structure of the series, which is of the Nb_3O_7F [7] type. Finally, the structures of Nb_2O_5, $Nb_{31}O_{77}F$ and $Nb_{17}O_{42}F$ are given in Fig. 3 by a conventional octahedral drawing.

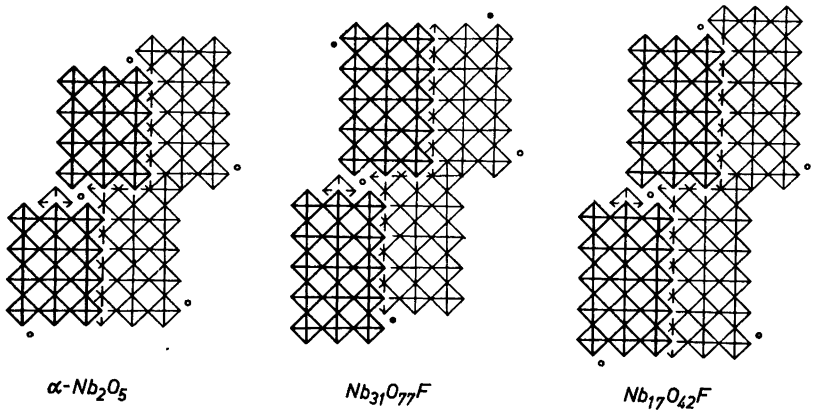


Fig. 3. The structures of α-Nb_2O_5, $Nb_{31}O_{77}F$ and $Nb_{17}O_{42}F$ drawn as a set of idealized octahedra. The circles are niobium atoms in tetrahedral positions. In Nb_2O_5 and $Nb_{17}O_{42}F$ all the metal atoms in tetrahedral positions are at $y = 0.25$. In $Nb_{31}O_{77}F$ the corresponding atoms are alternately at 0.25 and 0.75 according to the space group $C2$. This is demonstrated in the figure by open and filled circles.

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