

The Crystal Structure of $\text{Nb}_3\text{O}_7\text{F}$

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The oxide fluoride $\text{Nb}_3\text{O}_7\text{F}$ was first found in "Specpure" niobium pentoxide. The compound was then synthesized by the reaction of $\alpha\text{-Nb}_2\text{O}_5$ and NbO_2F . Its crystal structure has been determined, using single-crystal methods. The space group is $Cmmm$, with the unit-cell dimensions:

$$a = 20.67 \text{ \AA}; b = 3.833 \text{ \AA}; c = 3.927 \text{ \AA}$$

The structure consists of blocks of the ReO_3 -structure type which are fused together by means of octahedra sharing edges. The blocks are infinite in the b - and c -directions and limited to three octahedra in the a -direction. A hypothetical structure of this type has earlier been described by Wadsley as being the end member of his homologous series of mixed oxides of titanium and niobium, following the general formula $\text{M}_{3n}\text{O}_{8n-3}$.

In his study of the mixed oxides of titanium and niobium, Wadsley predicted a compound of the general composition M_3X_8 with a structure that would form the parent member of his homologous series $\text{M}_{3n}\text{O}_{8n-3}$.^(1,4) Since then another homologous series has been proposed with the ternary oxide $\text{NaNb}_{13}\text{O}_{33}$ as the only known member.² The general formula for this homologous series is $\text{NaM}_{3n+1}\text{O}_{8n+1}$ and its end member is also identical with the one predicted by Wadsley. In a recent paper, Roth, Wadsley, and Gatehous³ present a new remarkable homologous series of the general formula $\text{M}_{3n+1}\text{O}_{8n-2}$, with the separate members $\text{Nb}_{22}\text{O}_{54}$, $\text{TiNb}_{24}\text{O}_{62}$ and the hightemperature form of Nb_2O_5 corresponding to $n = 7, 8, \text{ and } 9$, respectively. The parent member of this series is again the hypothetical structure of the general composition M_3X_8 .

This compound of the general composition M_3X_8 has now been found as a niobium oxide fluoride with the composition $\text{Nb}_3\text{O}_7\text{F}$. Its detailed crystal structure will now be reported.

Similar X-ray studies on a system of metal oxide-metal fluoride, performed in order to obtain compounds of complex compositions but wanted structures were done by Aurivillius on the $\text{BiF}_3\text{-Nb}_2\text{O}_5$, $\text{BiF}_3\text{-Ta}_2\text{O}_5$ and $\text{BiF}_3\text{-TiO}_2$ and also the $\text{BiF}_3\text{-Bi}_2\text{O}_3$ system.⁵⁻⁷ Analogous studies on the $\text{NbO}_2\text{F-Nb}_2\text{O}_5$ system have been performed and are reported in a separate paper.⁸

Table 1. Crystallographic constants for Nb₃O₇F.

Unit-cell dimensions $a = 20.67 \text{ \AA}$
 $b = 3.833 \text{ \AA}$
 $c = 3.927 \text{ \AA}$

Systematic absent reflexions: hkl with $h + k$ odd.

Possible space groups: $Cmmm$, $C222$, $Cmm2$ and $C2mm$ (Nos. 65, 21, 35, and 38).

$d_{\text{obs}} = 4.27$, $d_{\text{calc}} = 4.37$, $Z = 2$.

EXPERIMENTAL

In a sample of "Specpure" niobium pentoxide, bought from Johnson, Matthey & Co. Ltd. during the year 1961, small, colourless and rectangular plates of crystals were found. Single-crystal X-ray studies showed the crystals to be of orthorhombic symmetry and the crystallographic constants are given in Table 1.

The reciprocal lattice clearly showed the presence of a subcell orientation and from the unit-cell dimensions a trial structure was obtained, which had the general composition M_3X_8 . An impurity that could be present in "Specpure" niobium pentoxide was fluorine and the trial composition would then be Nb₃O₇F. α -Nb₂O₅ and NbO₂F were therefore mixed in the mole ratio 1:1 and heated in sealed platinum tubes at 800°C for two days. Beautiful, colourless crystals had formed and they were of the same shape as the crystals that had been found in the commercial sample of Nb₂O₅. Guinier powder patterns and single-crystal studies on the synthesized crystals showed them to be identical with the crystals found in the "Specpure" niobium pentoxide sample. The density measurement given in Table 1 was made on the synthesized crystals of the composition Nb₃O₇F. A complete phase analysis of the system α -Nb₂O₅-NbO₂F has been performed at temperatures 500–800°C and is reported in a separate paper.⁸

The $hk0$, hkl , and $hk2$ reflections were recorded with CuK radiation on an integrating Nonius Weissenberg goniometer using the multiple-film technique, and estimations of intensity were made visually by means of a standard scale. The Nb⁵⁺ scattering curve used was derived from the tables of Thomas and Umeda.⁹ For O²⁻ the scattering curve given by Suzuki¹⁰ was used. Random occupancy of the anion sites was assumed and one F⁻ was simply treated as if it was one O²⁻ due to the small difference in scattering between the two elements.

STRUCTURE DETERMINATION

The trial structure obtained from the subcell and unit-cell dimensions was tested by means of structure factor calculations. A very good general agreement was obtained and 124 independent reflections from $hk0$, hkl , and $hk2$ data were used in several least-squares cycles using the Åsbrink-Brändén program written for the Swedish computer FACIT.¹¹ The least-squares procedure

Table 2. Atomic parameters in Nb₃O₇F. Space group $Cmmm$ (0, 0, 0; $\frac{1}{2}$, $\frac{1}{2}$, 0) +

Atom	Position	x	y	z	B	σB
2 Nb ₁	2a	0	0	0	1.24	0.09
4 Nb ₂	4g	0.1836 ± 0.00015	0	0	0.41	0.05
2 O ₁	2b	$\frac{1}{2}$	0	0	2.05	0.95
2 O ₂	2d	0	0	$\frac{1}{2}$	2.30	0.99
4 O ₃	4g	0.094 ± 0.0015	0	0	1.90	0.64
4 O ₄	4g	0.710 ± 0.001	0	0	0.52	0.45
4 O ₅	4h	0.189 ± 0.001	0	$\frac{1}{2}$	0.55	0.46

stopped at an R factor of 10 %. The space group with the highest symmetry, $Cmmm$, was used, as there was no geometrical reason to use any of the space groups of lower symmetry (Table 1). The final R value obtained also supports the choice of space group, and the structure was thus not tested for any of the lower space groups.

The original data were now corrected for absorption by means of a program written for FACIT by Werner.¹¹ The new data were again processed in a least-squares procedure and this time the refinement stopped at an R factor of 7.4 %. Only minor shifts of the atomic coordinates were observed, while the temperature factors changed considerably after the absorption correction.

Table 3. Weight analysis used in the last cycle of the refinement of Nb₃O₇F. $w =$ weighting factor. $\Delta = ||F_o| - |F_c||$.

Interval $\sin \Theta$	$w\Delta^2$	Number of independent reflections	Interval F_o	$w\Delta^2$	Number of independent reflections
0.00–0.46	0.84	28	0–34	0.50	26
0.46–0.58	1.22	17	34–68	0.77	41
0.58–0.66	1.11	21	68–102	1.13	28
0.66–0.73	1.27	12	102–136	1.50	22
0.73–0.79	0.78	8	136–204	1.82	7
0.79–0.84	1.66	11			
0.84–0.88	0.28	5			
0.88–0.92	0.60	12			
0.92–0.99	0.67	10			

Atomic coordinates with standard deviations and temperature factors are given in Table 2. The weight analysis for the last cycle of refinement is given in Table 3.

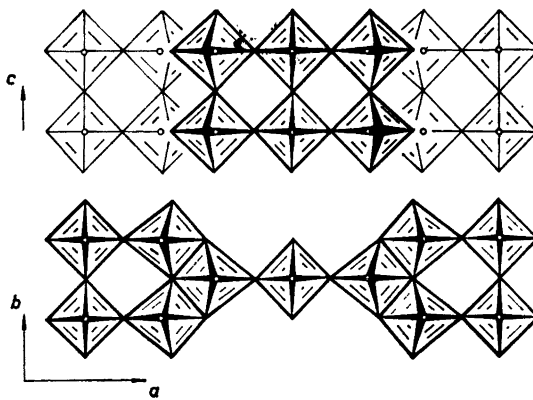


Fig. 1. The crystal structure of Nb₃O₇F.

DISCUSSION

The structure of $\text{Nb}_3\text{O}_7\text{F}$ is illustrated in Fig. 1. Interatomic distances with their estimated standard deviations are given in Table 4. The oxygen and fluorine atoms are assumed to substitute each other in a random way. The structure consists of blocks of the ReO_3 -structure type which are fused together by means of octahedra having edges in common. The blocks are infinite in the b - and c -directions and limited to three octahedra in the a -direc-

Table 4. Interatomic distances in the two $\text{Nb}(\text{O},\text{F})_6$ octahedra in $\text{Nb}_3\text{O}_7\text{F}$ and in the $\text{Nb}(\text{O},\text{F})_6$ octahedron in NbO_2F .

Distance	Å	$\text{Nb}_3\text{O}_7\text{F}$	σ Å	Mean value Å
2 Nb_1-O_1	1.917		0.001	
2 Nb_1-O_2	1.964		0.001	1.939
2 Nb_1-O_3	1.937		0.004	
4 O_1-O_2	2.74		0.001	
4 O_1-O_3	2.73		0.03	2.74
4 O_2-O_3	2.76		0.03	
Nb_2-O_3	1.86		0.03	
2 Nb_2-O_4	1.99		0.01	1.995
$\text{Nb}_2-\text{O}_4'$	2.20		0.03	
2 Nb_2-O_5	1.96		0.01	
2 O_3-O_4	3.07		0.04	
2 O_3-O_5	2.79		0.04	
2 O_4-O_5	2.54		0.06	2.81
4 $\text{O}_4-\text{O}_5'$	2.80		0.02	
2 $\text{O}_4-\text{O}_5'$	2.86		0.04	
		NbO_2F		
6 $\text{Nb}-\text{O}$		1.949 ± 0.001		
12 $\text{O}-\text{O}$		2.755 ± 0.001		

Table 5. Comparison between the atomic coordinates of $\text{Nb}_3\text{O}_7\text{F}$ and those of an M_3O_8 unit cut out of $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$.

	$\text{Nb}_3\text{O}_7\text{F}$			M_3O_8		
	x	y	z	x	y	z
Nb_1	0	0	0	0	0	0
Nb_2	0.1836	0	0	0.1848	0	0
O_1	$\frac{1}{2}$	0	0	0.500	0	0
O_2	0	0	$\frac{1}{2}$	0	0	0.500
O_3	0.094	0	0	0.093	0	0
O_4	0.210	$\frac{1}{2}$	0	0.214	0.500	0
O_5	0.189	0	$\frac{1}{2}$	0.190	0	0.500

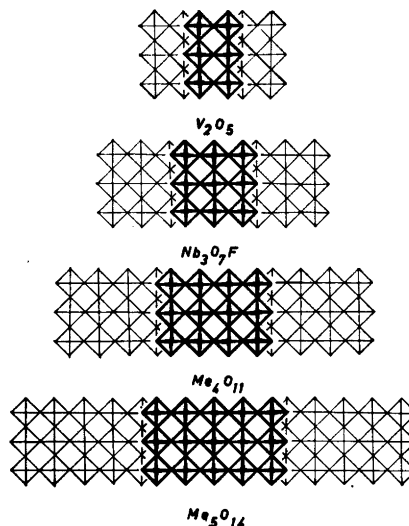


Fig. 2. The geometrical principles of the homologous series $M_n O_{3n-1}$, with the two known members $V_2 O_5$ ($n = 2$) and $Nb_3 O_7 F$ ($n = 3$).

tion. There are two kinds of $Nb(O,F)_6$ octahedra in the structure. One is almost undistorted with a mean value of the metal-anion distance of 1.94 Å, which is very close to the metal-anion distance of 1.95 Å observed for $NbO_2 F$.⁸ The same is also true for the anion-anion distances observed in the octahedron. The other $Nb(O,F)_6$ octahedron is more distorted due to the metal-metal repulsion caused by the edge sharing.

The structure of $Nb_3 O_7 F$ forms the end number of Wadsley's homologous series $M_{3n} O_{8n-3}$ with the two known members $TiNb_2 O_7$ and $Ti_2 Nb_{10} O_{29}$ ($n = 3$ and 4).¹ If an $M_3 O_8$ unit is cut out from the structure of the orthorhombic form of $Ti_2 Nb_{10} O_{29}$ and compared with $Nb_3 O_7 F$, an excellent agreement between the two sets of parameters is obtained. This is demonstrated in Table 5.

If the size of the ReO_3 -structure type blocks are increased or decreased in the finite a -direction a new homologous series is formed. This is demonstrated in Fig. 2. The general formula is $M_n O_{3n-1}$, where O stands for oxygen or a mixture of fluorine and oxygen. $n = 3$ gives $Nb_3 O_7 F$, $n = 2$ gives in idealized form the structure of $V_2 O_5$,¹³ and $n = 1$ corresponds to a so far unknown structure of the composition MO_2 . The end member ($n = \infty$) will naturally become a structure of ReO_3 type ($NbO_2 F$). Attempts to make members with $n > 3$, but still finite, were unsuccessful in the $Nb_2 O_5 - NbO_2 F$ system.⁸

The variation of the temperature factors (Table 2) of the atoms in the $Nb_3 O_7 F$ lattice is understood from the structure. In the undistorted $Nb(O,F)_6$ octahedron, which is situated right between the shear planes, all the atoms (Nb_1 , O_1 , O_2 , and O_3) have considerable thermal vibrations. In the distorted $Nb(O,F)_6$ octahedron, which forms part of the shear plane, all the atoms (Nb_2 , O_4 , and O_5) have much less thermal vibrations, as this part of the structure is the much denser one.

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REFERENCES

1. Wadsley, A. D. *Acta Cryst.* **14** (1961) 660, 664.
2. Andersson, S. *Intern. Union of Crystallography*, Rome 1963.
3. Roth, R. S., Wadsley, A. D. and Gatehouse, B. M. *Naturwiss.* **51** (1964) 262.
4. Wadsley, A. D. *Non-stoichiometric Compounds*, Academic Press, New York 1964, pp. 98–209.
5. Aurivillius, B. *Arkiv Kemi* **5** (1952) 31.
6. Aurivillius, B. *Acta Chem. Scand.* **9** (1955) 1206.
7. Aurivillius, B. and Lundqvist, T. *Acta Chem. Scand.* **9** (1955) 1209.
8. Andersson, S. and Åström, A. *Acta Chem. Scand.* **18** (1964) 2233.
9. Thomas, L. H. and Umeda, K. *J. Chem. Phys.* **26** (1957) 293.
10. Suzuki, T. *Acta Cryst.* **13** (1960) 279.
11. Åsbrink, S. and Brändén, C. *List of Crystallographic Computer Programs* (1962). Accession number 6023.
12. Werner, P. E. *List of Crystallographic Computer Programs* (1962). Accession number 6019.
13. Byström, A., Wilhelmi, K. A. and Brotzen, O. *Acta Chem Scand.* **4** (1950) 1119.

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