

Mauer, in the press). The bond distances observed in coordinated imidazole are in substantial agreement with those found for corresponding bonds in coordinated biimidazole. Related pairs agree to within two standard deviations of the imidazole bond distances. The observed distances in the imidazole ring, moreover, are in close agreement with the values calculated by Dewar & Gleicher (1966) and with those found by Lundberg (1966) in diimidazolezinc(II) dichloride. The shortest observed and calculated distances in the imidazole ring is between atoms involved in the classical C-N double bond.

Table 5. Distances from the ring atoms to the least-squares planes of the imidazole ring

The equation of the plane in direct space is given by  $PX + QY + RZ = S$  ( $P = 11.385$ ,  $Q = -5.0896$ ,  $R = 5.6823$  and  $S = 0.16597$ ).

N(1)	0.00574 Å
N(2)	0.00593
C(1)	-0.00742
C(2)	-0.00221
C(3)	-0.00204

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## The Crystal Structure of $\text{NaNbO}_2\text{F}_2$

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$\text{NaNbO}_2\text{F}_2$ , a new niobium oxide fluoride, is monoclinic, with  $a = 8.063$ ,  $b = 5.405$ ,  $c = 7.626$  Å,  $\beta = 101.70^\circ$ , space group  $P2_1/c$ . The structure, refined by the least-squares method, contains layers of corner-sharing  $\text{NbO}_4\text{F}_2$  octahedra. The structure of the layers with the composition  $(\text{NbO}_2\text{F}_2)_n^{2-}$  is related to the  $\text{PdF}_3$  structure type. The structure of  $\text{NaNbO}_2\text{F}_2$  is also related to the  $\alpha\text{-PbO}_2$  structure type. The anion arrangement is probably ordered.

### Introduction

The substitution of  $\text{F}^-$  for  $\text{O}^{2-}$  in niobium oxides has been useful in making compounds of simple and predictable structures, which can serve as model substances for the study of the principles of synthesis, non-stoichiometry, and possible mechanisms of reaction (Andersson, 1967). Preparative and structural studies have been made on the  $\text{NaNbO}_3\text{-Nb}_2\text{O}_5$ ,  $\text{NaNbO}_3\text{-Nb}_2\text{O}_5\text{-H}_2\text{O}$  and  $\text{NaF-Nb}_2\text{O}_5$  systems. The present paper reports the crystal structure of  $\text{NaNbO}_2\text{F}_2$ , a new compound which has been prepared in the  $\text{NaF-NbO}_2\text{F}$  system.

A number of computer programs were written at the NBS specifically for this problem. We would like to acknowledge the use of the X-ray 63 system developed at the Universities of Maryland and Washington. The authors wish to thank Professor J. Stewart for assistance in using the system. Thanks are also due to Mrs Marlene Morris for determining the lattice parameters with the powder method.

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### Experimental

Heating a mixture of  $\text{NaF}$  and  $\text{NbO}_2\text{F}$  in the mole ratio 1:1 in a sealed platinum capsule for one day at  $600^\circ\text{C}$  resulted in a product consisting of colourless plate-shaped crystals. Single-crystal X-ray studies showed the crystals to be of monoclinic symmetry and the crystallographic constants are given in Table 1. The Hagg-Guinier powder pattern is given in Table 2. The  $h0l$ ,  $h1l$ ,  $h2l$  and  $h3l$  reflexions were registered on multiple films by the integrating Weissenberg method using  $\text{Cu K}\alpha$  radiation and were measured by means of a calibrated film strip. Because of the small crystal

used,  $0.05 \times 0.04 \times 0.02$  mm, no absorption corrections were considered necessary. All calculations were performed on an IBM 7090 computer, with the *Crystal Structure Calculations System, X-ray 63* (Stewart & High, 1964). The  $\text{Nb}^{5+}$  scattering curve used was derived from the tables of Thomas & Umeda (1957). For  $\text{Na}^+$  and  $\text{O}^{2-}$  the scattering curves given by Freeman (1959) and Suzuki (1960) were used. The  $\text{F}^-$  scattering curve was taken from *International Tables for X-ray Crystallography* (1962).

Table 1. *Crystallographic data for*  $\text{NaNbO}_2\text{F}_2$ 

Symmetry: monoclinic.  
Unit-cell dimensions:  $a = 8.013 \pm 0.002$  Å  
 $b = 5.405 \pm 0.002$   
 $c = 7.626 \pm 0.002$   
 $\beta = 101.70 \pm 0.05^\circ$

Systematically absent reflexions

$$h0l, l \neq 2n$$

$$0k0, k \neq 2n$$

Space group  $P2_1/c$   
 $Z = 4$

### Structure determination

Approximate niobium coordinates were obtained from the Patterson projection on to (010). From the single-crystal data some similarities of this structure and the structure of  $\alpha\text{-PbO}_2$  were recognized, and with the use of this information, it was easy to derive approximate

Table 2. *Powder pattern of*  $\text{NaNbO}_2\text{F}_2$  (Cu  $K\alpha_1$ )

Intensity	$\sin^2 \theta$ (obs)	$hkl$	$\sin^2 \theta$ (calc)
<i>m</i>	0.00959	100	0.00965
<i>vst</i>	0.03000	110	0.02997
<i>w</i>	0.03859	200	0.03862
<i>w+</i>	0.04264	002	0.04264
<i>m</i>	0.04387	10 $\bar{2}$	0.04389
<i>vst</i>	0.05901	210	0.05893
<i>vst</i>	0.06302	01 $\bar{2}$	0.06295
<i>vw</i>	0.06412	11 $\bar{2}$	0.06420
<i>w</i>	0.06443	20 $\bar{2}$	0.06446
<i>st</i>	0.08098	{ 112	{ 0.08100
		{ 020	{ 0.08124
<i>w</i>	0.08474	21 $\bar{2}$	0.08477
<i>vw</i>	0.08699	300	0.08690
<i>w</i>	0.09083	120	0.09089
<i>vw</i>	0.09804	202	0.09806
<i>m</i>	0.10573	{ 31 $\bar{1}$	{ 0.10527
		{ 12 $\bar{1}$	{ 0.10575

positions for the anions as well as for the sodium atoms. The first electron density projection on to (010) showed all the atoms in the expected positions. For all the atoms the  $4(e)$  position in space group  $P2_1/c$  was chosen, and the data were processed by a full-matrix least-squares refinement. The very strong 110, 210, 120, 130, 012, 222, 320 and 230 reflexions were omitted in the calculations. Of the four anions two (1 and 2) are shared between two Nb and one Na, and the other two (3 and 4) between one Nb and three Na. It was considered well worth trying an ordered arrangement of the anions in a least-squares refinement. Atoms

Table 3. *Fractional atomic parameters*

Space group  $P2_1/c$ . All atoms in the general position  $4(e)$ .

Alt. 1. All atoms treated as oxygens		Alt. 2. Ordered arrangement of oxygen and fluorine		Coordinates for atoms in an ideal, hexagonal close-packed arrangement	
Nb	<i>x</i>	$0.1555 \pm 2$	$0.1554 \pm 2$		0.1875
	<i>y</i>	$0.2654 \pm 5$	$0.2655 \pm 5$		0.2500
	<i>z</i>	$0.3177 \pm 2$	$0.3176 \pm 2$		0.3125
	<i>B</i>	$1.14 \pm 5$	$1.10 \pm 5$		
Na	<i>x</i>	$0.3679 \pm 11$	$0.3685 \pm 11$		0.3125
	<i>y</i>	$0.7741 \pm 26$	$0.7750 \pm 25$		0.7500
	<i>z</i>	$0.1187 \pm 13$	$0.1187 \pm 12$		0.1875
	<i>B</i>	$2.47 \pm 18$	$2.42 \pm 17$		
O(1)	<i>x</i>	$0.1705 \pm 18$	$0.1721 \pm 17$		0.1875
	<i>y</i>	$0.1591 \pm 42$	$0.1561 \pm 39$		0.1250
	<i>z</i>	$0.0533 \pm 19$	$0.0545 \pm 19$		0.0625
	<i>B</i>	$1.39 \pm 30$	$1.34 \pm 29$		
O(2)	<i>x</i>	$0.0333 \pm 19$	$0.0351 \pm 18$		0.0625
	<i>y</i>	$0.5571 \pm 41$	$0.5546 \pm 38$		0.6250
	<i>z</i>	$0.2066 \pm 20$	$0.2084 \pm 19$		0.1875
	<i>B</i>	$1.38 \pm 27$	$1.24 \pm 24$		
O(3)	<i>x</i>	$0.3750 \pm 16$	$0.3760 \pm 15$		0.4375
	<i>y</i>	$0.4497 \pm 36$	$0.4513 \pm 33$		0.3750
	<i>z</i>	$0.3143 \pm 16$	$0.3142 \pm 16$		0.3125
	<i>B</i>	$0.53 \pm 23$	$1.86 \pm 24$		
O(4)	<i>x</i>	$0.3164 \pm 16$	$0.3166 \pm 16$		0.3125
	<i>y</i>	$0.9835 \pm 38$	$0.9827 \pm 34$		0.8750
	<i>z</i>	$0.3775 \pm 19$	$0.3793 \pm 18$		0.4375
	<i>B</i>	$0.95 \pm 26$	$2.16 \pm 26$		

Table 4. Observed and calculated structure factors

For unobserved reflexions (indicated by an asterisk) mod  $F_0$  is the estimated threshold value.

$h_1 k_1 l_1$	$F_{obs}$	$F_{calc}$	$h_1 k_1 l_1$	$F_{obs}$	$F_{calc}$	$h_1 k_1 l_1$	$F_{obs}$	$F_{calc}$	$h_1 k_1 l_1$	$F_{obs}$	$F_{calc}$
1 000 030	4 938 96v	4 176v 57	0 100v 7	0 100v 7	0 100v 7	5 281 24v	7 178v 107	1 007 22v	0 09v 78v	0 09v 78v	$h_1 k_1 l_1$
2 000 060	9 876 88v	7 176v 6	0 100v 7	0 100v 7	0 100v 7	0 07v 04v	0 177v 04v	2 175v 15v	0 09v 42v	0 09v 42v	4 09v 28v
3 000 090	14 814 81v	6 18v 17v	1 100v 17v	1 100v 17v	1 100v 17v	7 593 500v	5 165v 51v	3 170v 22v	1 218 26v	1 218 26v	6 235 300v
4 000 120	19 752 12v	5 193v 170v	2 120v 17v	2 120v 17v	2 120v 17v	0 161v 89v	4 140v 100v	4 176v 14v	2 300 29v	2 300 29v	7 576 55v
5 000 150	24 690 15v	4 204v 113v	3 150v 28v	3 150v 28v	3 150v 28v	0 067v 45v	3 136v 138v	5 162v 31v	3 350 465v	3 350 465v	8 306 353v
6 000 180	29 628 18v	3 596v 617v	4 180v 128v	4 180v 128v	4 180v 128v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	9 497 413v
7 000 210	34 566 21v	2 88v 30v	5 177v 23v	5 177v 23v	5 177v 23v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	10 688 487v
8 000 240	39 504 24v	0 177v 04v	6 177v 04v	6 177v 04v	6 177v 04v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	11 879 591v
9 000 270	44 442 27v	7 101v 84v	7 101v 84v	7 101v 84v	7 101v 84v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	12 107 695v
10 000 300	49 380 30v	8 181v 130v	8 181v 130v	8 181v 130v	8 181v 130v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	13 298 800v
11 000 330	54 318 33v	1 81v 92v	9 171v 290v	9 171v 290v	9 171v 290v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	14 499 905v
12 000 360	59 256 36v	4 438v 460v	10 195v 220v	10 195v 220v	10 195v 220v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	15 700 1010v
13 000 390	64 194 39v	8 162v 70v	11 219v 54v	11 219v 54v	11 219v 54v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	16 901 1115v
14 000 420	69 132 42v	7 295v 601v	12 243v 88v	12 243v 88v	12 243v 88v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	17 102 1220v
15 000 450	74 070 45v	0 177v 04v	13 267v 122v	13 267v 122v	13 267v 122v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	18 303 1325v
16 000 480	79 008 48v	6 552v 388v	14 291v 156v	14 291v 156v	14 291v 156v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	19 504 1430v
17 000 510	83 946 51v	8 181v 130v	15 315v 190v	15 315v 190v	15 315v 190v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	20 705 1535v
18 000 540	88 884 54v	9 271v 240v	16 339v 224v	16 339v 224v	16 339v 224v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	21 906 1640v
19 000 570	93 822 57v	10 369v 278v	17 363v 258v	17 363v 258v	17 363v 258v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	22 107 1745v
20 000 600	98 760 60v	11 459v 316v	18 387v 292v	18 387v 292v	18 387v 292v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	23 308 1850v
21 000 630	103 698 63v	12 549v 354v	19 411v 326v	19 411v 326v	19 411v 326v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	24 509 1955v
22 000 660	108 636 66v	13 639v 392v	20 435v 360v	20 435v 360v	20 435v 360v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	25 710 2060v
23 000 690	113 574 69v	14 729v 430v	21 459v 394v	21 459v 394v	21 459v 394v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	26 911 2165v
24 000 720	118 512 72v	15 819v 468v	22 483v 428v	22 483v 428v	22 483v 428v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	28 112 2270v
25 000 750	123 450 75v	16 909v 506v	23 507v 462v	23 507v 462v	23 507v 462v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	29 313 2375v
26 000 780	128 388 78v	18 000v 544v	24 531v 496v	24 531v 496v	24 531v 496v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	30 514 2480v
27 000 810	133 326 81v	19 090v 582v	25 555v 530v	25 555v 530v	25 555v 530v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	31 715 2585v
28 000 840	138 264 84v	20 180v 620v	26 579v 564v	26 579v 564v	26 579v 564v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	32 916 2690v
29 000 870	143 202 87v	21 270v 658v	27 603v 598v	27 603v 598v	27 603v 598v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	34 117 2795v
30 000 900	148 140 90v	22 360v 696v	28 627v 632v	28 627v 632v	28 627v 632v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	35 318 2900v
31 000 930	153 078 93v	23 450v 734v	29 651v 666v	29 651v 666v	29 651v 666v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	36 519 3005v
32 000 960	158 016 96v	24 540v 772v	30 675v 700v	30 675v 700v	30 675v 700v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	37 720 3110v
33 000 990	162 954 99v	25 630v 810v	31 700v 734v	31 700v 734v	31 700v 734v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	38 921 3215v
34 000 1020	167 892 102v	26 720v 858v	32 724v 768v	32 724v 768v	32 724v 768v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	40 122 3320v
35 000 1050	172 830 105v	27 810v 906v	33 748v 802v	33 748v 802v	33 748v 802v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	41 323 3425v
36 000 1080	177 768 108v	28 900v 954v	34 772v 836v	34 772v 836v	34 772v 836v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	42 524 3530v
37 000 1110	182 706 111v	29 990v 1002v	35 796v 870v	35 796v 870v	35 796v 870v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	43 725 3635v
38 000 1140	187 644 114v	31 080v 1050v	36 820v 904v	36 820v 904v	36 820v 904v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	44 926 3740v
39 000 1170	192 582 117v	32 170v 1098v	37 844v 938v	37 844v 938v	37 844v 938v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	46 127 3845v
40 000 1200	197 520 120v	33 260v 1146v	38 868v 972v	38 868v 972v	38 868v 972v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	47 328 3950v
41 000 1230	202 458 123v	34 350v 1194v	39 892v 1006v	39 892v 1006v	39 892v 1006v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	48 529 4055v
42 000 1260	207 396 126v	35 440v 1242v	40 916v 1040v	40 916v 1040v	40 916v 1040v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	49 730 4160v
43 000 1290	212 334 129v	36 530v 1290v	41 940v 1074v	41 940v 1074v	41 940v 1074v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	50 931 4265v
44 000 1320	217 272 132v	37 620v 1338v	42 964v 1108v	42 964v 1108v	42 964v 1108v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	52 132 4370v
45 000 1350	222 210 135v	38 710v 1386v	43 988v 1142v	43 988v 1142v	43 988v 1142v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	53 333 4475v
46 000 1380	227 148 138v	39 800v 1434v	45 012v 1176v	45 012v 1176v	45 012v 1176v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	54 534 4580v
47 000 1410	232 086 141v	40 890v 1482v	46 036v 1210v	46 036v 1210v	46 036v 1210v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	55 735 4685v
48 000 1440	237 024 144v	41 980v 1530v	47 060v 1244v	47 060v 1244v	47 060v 1244v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	56 936 4790v
49 000 1470	241 962 147v	43 070v 1578v	48 084v 1278v	48 084v 1278v	48 084v 1278v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	58 137 4895v
50 000 1500	246 900 150v	44 160v 1626v	49 108v 1312v	49 108v 1312v	49 108v 1312v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	59 338 5000v
51 000 1530	251 838 153v	45 250v 1674v	50 132v 1346v	50 132v 1346v	50 132v 1346v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	60 539 5105v
52 000 1560	256 776 156v	46 340v 1722v	51 156v 1380v	51 156v 1380v	51 156v 1380v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	61 740 5210v
53 000 1590	261 714 159v	47 430v 1770v	52 180v 1414v	52 180v 1414v	52 180v 1414v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	62 941 5315v
54 000 1620	266 652 162v	48 520v 1818v	53 204v 1448v	53 204v 1448v	53 204v 1448v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	64 142 5420v
55 000 1650	271 590 165v	49 610v 1866v	54 228v 1482v	54 228v 1482v	54 228v 1482v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	65 343 5525v
56 000 1680	276 528 168v	50 700v 1914v	55 252v 1516v	55 252v 1516v	55 252v 1516v	0 132v 54v	2 123v 54v	6 138v 141v	0 138v 141v	0 138v 141v	66 544 5630v
57 000 1710	281 466 171v	51 790v 1962v	56 276v 1550v	56 276v 1550v	56 276v 155						

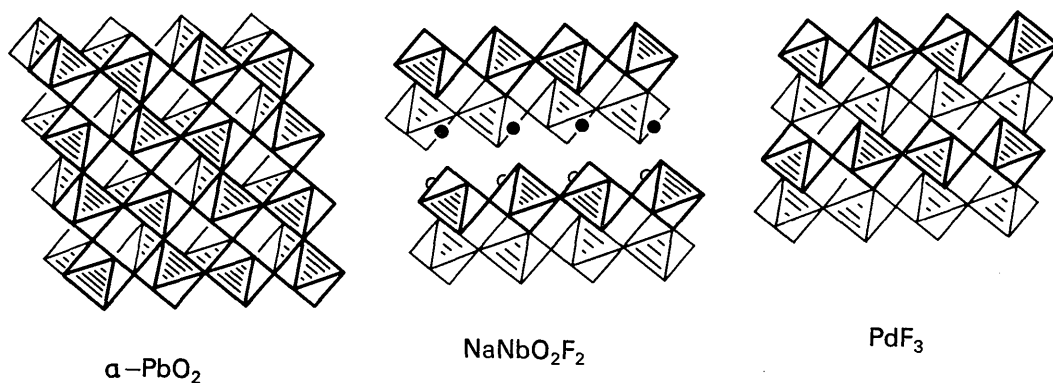


Fig. 3. The relationships between the  $\alpha\text{-PbO}_2$ ,  $\text{NaNbO}_2\text{F}_2$  and  $\text{PdF}_3$  structure types. The drawings of the structures are idealized.

### Description of the structure

The structure is shown in Fig. 1. The niobium atom has four nearest oxygen neighbours at an average distance of 1.94 Å, and two nearest fluorine neighbours at an average of 2.015 Å. Within this octahedron the average oxygen–oxygen distance is 2.82 Å, the corresponding value for oxygen–fluorine is 2.75 Å and for fluorine–fluorine 2.65 Å. The configuration of the anions around sodium can be described in two different ways.  $\text{F}_3^1$ ,  $\text{F}_3^{11}$ ,  $\text{F}_3^{111}$ ,  $\text{F}_4^1$ ,  $\text{F}_4^{11}$  and  $\text{F}_4^{111}$  form a trigonal prism and on the outside of this there is an oxygen atom  $\text{O}_1^1$ , which completes the sevenfold coordination of sodium. On the other hand, sodium can also be described as being situated in a distorted octahedron of  $\text{O}_1^1$ ,  $\text{O}_2^1$ ,  $\text{F}_3^1$ ,  $\text{F}_3^{11}$ ,  $\text{F}_4^1$  and  $\text{F}_4^{11}$ . The sodium–fluorine distances within this octahedron are 2.26, 2.23, 2.36 and 2.22 Å with an average of 2.30 Å. The errors for the Nb–(O, F), Na–(O, F) and (O, F)–(O, F) distances are 0.015, 0.020 and 0.025 Å respectively.

The anion arrangement of this structure is approximately hexagonally close-packed. The ideal coordinates for atoms in such an arrangement are given in Table 3. The relationships between the real monoclinic cell of  $\text{NaNbO}_2\text{F}_2$  and the hexagonal are:

$$\begin{aligned} \mathbf{a} &= 2\mathbf{a}_{\text{hex}} + \mathbf{c}_{\text{hex}} \\ \mathbf{b} &= \mathbf{a}_{\text{hex}} + \mathbf{b}_{\text{hex}} \\ \mathbf{c} &= -2\mathbf{a}_{\text{hex}} + \mathbf{c}_{\text{hex}} \end{aligned}$$

Some different ways of joining octahedra formed by a hexagonal close-packed arrangement of anions are

given in Fig. 2. The projection axis is the same as the  $b$  axis of  $\text{NaNbO}_2\text{F}_2$ .

If sodium is situated in an octahedron formed by the hexagonal close-packed arrangement of anions, the structure can be described as an ordered  $\alpha\text{-PbO}_2$  structure. The cation ordering, different from that of columbite, is described in an idealized drawing in Fig. 3.

Another way of describing this structure is to relate it to the  $\text{PdF}_3$  structure type (Hepworth, Jack, Peacock & Westland, 1957), which is demonstrated in Fig. 3. Here it can be seen that blocks of the  $\text{PdF}_3$  structure type form layers in the  $\text{NaNbO}_2\text{F}_2$  structure. The composition of these layers is  $(\text{NbO}_2\text{F}_2)_n^{n-}$ , and they are held together by the sodium ions. The niobium anion octahedra all share corners. The ordering of the fluorine and oxygen atoms found is quite natural, with the fluorine atoms bridging the sodium ions and the layers.

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