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The Crystal Structure of $NaTi_2Al_5O_{12}$

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$NaTi_2Al_5O_{12}$, a new compound prepared by solid-state reaction, crystallizes as colourless orthorhombic needles with the unit-cell dimensions $a = 9{\cdot}080$, $b = 15{\cdot}519$, $c = 2{\cdot}919$ Å, space group *Pbam*. The composition was deduced from the structure analysis, which proceeded by Patterson and Fourier methods to refinement of three-dimensional data by the method of least squares. The structure contains double strings of octahedra, one with aluminum and the other titanium joined by corners into sheets. These are further cross-linked by two additional aluminum polyhedra, an octahedron and a tetrahedron, while sodium occupies a flattened octahedral position between the double strings. The temperature factor for Na is anomalous, and the possible reasons for this are evaluated.

Introduction

Examination of alkali titanates in this laboratory showed that a characteristic and unifying feature for three compounds, $Na_2Ti_3O_7$, $Na_2Ti_6O_{13}$ and Ti_3O_5 was a condensed group of Ti–O octahedra sharing edges, three wide, and extending as an infinite zigzag unit throughout the structure of each one (Andersson & Wadsley, 1962*a*).

Additional arrangements of these groups can be devised which might represent hitherto unknown chemical compounds, the compositions being determined by counting atoms within the unit cells of their predetermined structures. In the course of unsuccessful attempts to prepare a fourth related phase $Na_2Ti_4Al_2O_{12}$, isostructural with a 'bronze' $Na_2Ti_6O_{12}$, we isolated a number of colourless orthorhombic needles which were formed together with a second aluminotitanate belonging to another bronze structure type, Na_xTiO_2 (Andersson & Wadsley, 1962*b*; Bayer & Hoffmann, 1965). These proved to be an unsuspected new phase with the ideal composition $NaTi_2Al_5O_{12}$.

Experimental

The compound is readily made by heating an intimate mixture of Na_2CO_3, Al_2O_3 and TiO_2 (anatase) in the molar ratio 1:5:4, first at 800 °C in air and then in a sealed capsule at 1300 °C for 48 hours.

It is characterized by its powder pattern (Table 1). The crystallographic data, summarized in Table 2, were determined from a Guinier film internally calibrated with potassium chloride, and the space group alternatives from single-crystal photographs. Intensity data *hkl* for the levels $l = 0, 1, 2$, were obtained by the integrated Weissenberg technique using filtered copper radiation, the crystal measuring 0·1 × 0·02 × 0·015 mm. Corrections for absorption were found to be unnecessary. Intensities were measured visually with a standard scale, and the reduction to structure amplitudes, and all subsequent computing, was carried out on the Division's Elliott 803 computer using the programming system devised by Daly, Stephens & Wheatley (1963) and kindly made available to us by Dr P. J. Wheatley. Interlayer scaling for the three levels of data was adjusted after each least-squares refinement cycle, and the scaled observed data and the structure amplitudes calculated from the final model are listed in Table 3. Scattering curves for non-ionized atoms, corrected for the real and imaginary components of the anomalous scattering for Cu $K\alpha$, were taken from *International Tables for X-ray Crystallography* (1962, p. 201 *et seq.*).

Table 1. *Powder pattern of* $NaTi_2Al_5O_{12}$, Cu $K\alpha_1$

I (obs)	$\sin^2\theta$ (obs)	$\sin^2\theta$ (calc)	*hkl*
mw	0·00964	0·00966	110
w	0·00984	0·00985	020
mw	0·01703	0·01705	120
m	0·02938	0·02937	130
vw	0·03937	0·03942	040
s	0·06823	0·06820	240
m	0·08699	0·08694	330
m	0·09842	0·09843	201
mw	0·09898	0·09901	131
vw	0·10832	0·10828	221
w	0·10906	0·10906	041
m	0·12068	0·12060	231
m	0·14952	0·14950	270
mw	0·17375	0·17383	341
ms	0·20281	0·20383	460

Table 2. *Crystallographic data for* $NaTi_2Al_5O_{12}$

Symmetry:	orthorhombic
Unit-cell dimensions	$a = 9{\cdot}080 \pm 0{\cdot}005$ Å $b = 15{\cdot}519 \pm 0{\cdot}005$ $c = 2{\cdot}919 \pm 0{\cdot}002$
Systematically absent reflexions	$0kl$, $k \neq 2n$ $h0l$, $h \neq 2n$
Possible space groups	*Pba*2 (no. 32) *Pbam* (no. 55)
D_x	3·60 g.cm^{-3}
Z	2
μ_c	114 cm^{-1}

Structure determination

The c-axis length of 2·92 Å corresponds in all probability to an oxygen-to-oxygen distance which will be an octahedral or tetrahedral edge. As all the atoms should be resolved in projection on to (001), where both space group alternatives *Pbam* and *Pba*2 are centred, the structure determination by Fourier methods was confined to the $hk0$ level, and all the data were used subsequently for the refinement by least-squares.

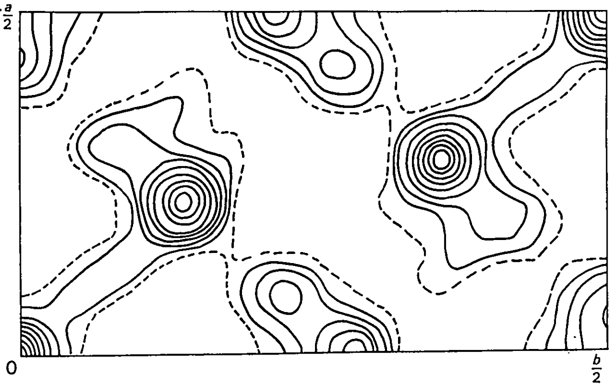

Fig. 1. Projection of the Patterson function, $P(u,v)$, positive regions only. The zero contour is dotted.

Apart from the question of chemical composition, which at this stage was uncertain, the interpretation of the Patterson function, $P(u,v)$, shown in Fig. 1, proved unexpectedly troublesome. An examination of it suggested a trial structure where the approximate locations of three metal atoms in general fourfold positions, A at (0·22, 0·14), B at (0, 0·29) and C at (0·28, 0·36), all centred about the point $(\frac{1}{4},\frac{1}{4})$, were determined from the strongest vector interactions when an additional metal was placed in the special twofold site at (0,0). Because the exact composition was unknown, and because it did not seem feasible at this stage to attempt to distinguish between any of these four positions, an averaged scattering curve for aluminum and titanium was used for calculating structure factors with this model. This had the effect of retaining the additional symmetry elements, to make the plane group *cmm* rather than the correct one *pgg*. While this resulted in poor overall agreement between the observed and calculated structure factors (because in *cmm* the terms F_{hk0} are zero when $h+k=2n+1$), a two-dimensional

Table 3. *Observed and calculated structure factors*

h	k	l	F_o(x100)	F_c(x100)
0	2	0	-9397	-10064
0	4	0	-11735	-13940
0	6	0	11072	12614
0	8	0	14777	10959
0	14	0	11657	11410
0	18	0	-6043	-5770
1	1	0	5770	4421
1	2	0	-6979	-7766
1	3	0	9630	9421
1	5	0	-3627	-4053
1	13	0	5380	5999
2	0	0	-1676	-2959
2	2	0	4639	5424
2	3	0	3315	3098
2	4	0	25536	25998
2	7	0	-13138	-14456
2	8	0	-5909	-7966
2	10	0	16413	17692
2	13	0	6667	6957
2	16	0	9291	5514
2	18	0	4951	3239
3	1	0	-8070	-9845
3	2	0	7758	8475
3	3	0	14620	15301
3	4	0	-6745	-7039
3	5	0	-6199	-6486
3	6	0	-9397	-10110
3	7	0	4095	3967
3	8	0	5341	5717
3	15	0	-5303	-4356
3	16	0	4951	4773
4	1	0	-3509	-3127
4	3	0	-4561	-4893
4	6	0	16179	17533
4	14	0	8460	8306
4	18	0	-3237	-3129
5	1	0	4095	5024
5	2	0	-5848	-6382
5	3	0	-6745	-7467
5	5	0	-6433	-6493
5	6	0	8850	8845
5	7	0	21053	20511
5	8	0	-7213	-7780
5	11	0	-5497	-5528
5	12	0	5497	6253
5	13	0	9319	9640
5	14	0	-3587	-3749
5	16	0	-2925	-2952
6	0	0	4639	3781
6	1	0	-3237	-3311
6	4	0	4873	5311
6	7	0	4639	5513
6	10	0	11735	11359
6	13	0	-3587	-3361
7	1	0	-5185	-4348
7	2	0	8227	8753
7	3	0	11150	12120
7	7	0	-5497	-4342
7	11	0	5146	5738
7	12	0	-4873	-3905
7	15	0	-3275	-2554
8	0	0	13411	12535
8	3	0	6745	6833
8	5	0	-3860	-4277
8	9	0	5107	4202
8	10	0	4873	4923
8	11	0	-3197	-2570
8	13	0	-2535	-1562
9	1	0	3792	4061
9	2	0	-5341	-4313
9	6	0	5029	4949
9	7	0	4873	4957
9	8	0	-4639	-3696
9	11	0	-3509	-1937
9	12	0	2885	3684
10	0	0	6745	6170
10	1	0	-5809	-5393
10	4	0	3157	2395
10	5	0	5303	5006
10	6	0	4172	2977
10	7	0	-3860	-3717
10	9	0	-3080	-2364
11	2	0	3470	3143
11	3	0	5303	5190
0	2	1	1383	846
0	4	1	13499	13041
0	6	1	-7500	-9933
0	8	1	-11323	-11756
0	10	1	26263	30639
0	14	1	-6529	-5757
0	16	1	2617	2976
0	18	1	3970	4346
1	2	1	2382	2707
1	3	1	3794	3351
1	4	1	5089	4223
1	7	1	5706	5973
1	9	1	3559	4309
1	11	1	3441	4556
1	13	1	5853	6349
1	17	1	2323	2292
2	0	1	26029	20964
2	2	1	-9147	-9064
2	3	1	18617	17784
2	4	1	-7147	-9607
2	5	1	-2059	-2724
2	6	1	12617	13833
2	14	1	8677	9764
2	17	1	-3853	-3044
2	18	1	-5029	-4818
3	1	1	7147	8521
3	2	1	-7265	-7854
3	3	1	5647	4527
3	4	1	8295	9646
3	5	1	-5264	-5422
3	6	1	8117	8365
3	7	1	17234	17556
3	8	1	-4471	-4612
3	10	1	-2795	-2992
3	11	1	-3559	-4692
3	13	1	7147	6547
3	16	1	-3441	-3303
3	17	1	2970	2667
4	4	1	15587	15237
4	8	1	-3853	-4922
4	16	1	4971	5376
5	1	1	-2441	-3713
5	3	1	20381	20996
5	6	1	-2706	-3553
5	7	1	-2795	-3038
5	8	1	2953	3781
5	9	1	2913	2042
5	10	1	2970	3566
5	11	1	5441	5355
5	12	1	-3501	-3446
5	15	1	-3206	-3712
5	16	1	3823	3872
6	3	1	-7265	-6799
6	6	1	4059	2979
6	14	1	2206	2786
7	1	1	7089	6405
7	2	1	-6147	-5114
7	6	1	4147	4078
7	7	1	10559	8624
7	8	1	-5764	-5396
7	12	1	6205	5207
7	13	1	9383	7311
8	0	1	6529	6502
8	1	1	-4117	-4207
8	5	1	4029	3453
8	7	1	-4735	-4050
8	10	1	8499	7441
9	2	1	5441	4326
9	3	1	5970	5131
9	6	1	-2471	-2311
9	4	1	-2617	-2771
9	8	1	3147	2708
9	9	1	2000	2614
10	0	1	-2265	-1580
10	1	1	2265	2154
10	3	1	5795	5640
10	4	1	3676	3339
10	5	1	-5983	-5132
10	6	1	2295	2412
0	2	2	-9181	-5637
0	4	2	-8741	-7467
0	6	2	8833	8050
0	8	2	5127	5487
0	14	2	7434	7686
1	1	2	5011	3260
1	2	2	-4125	-3335
1	3	2	8979	5527
1	13	2	3393	4174
1	14	2	1889	1596
1	7	2	3939	3772
2	0	2	-3296	-1980
2	2	2	2097	1675
2	3	2	2121	1591
2	4	2	14100	14052
2	7	2	-7249	-7092
2	8	2	-5710	-5620
2	10	2	10324	11137
2	13	2	4032	4419
2	14	2	2913	-3035
2	16	2	4125	4262
3	1	2	-5337	-4455
3	2	2	5384	4217
3	3	2	11909	10951
3	4	2	-3146	-3794
3	5	2	-2773	-3059
3	6	2	-5127	-4994
3	7	2	2867	2619
3	8	2	3296	3143
3	9	2	2307	2467
3	11	2	3100	3411
3	12	2	-2074	-2441
3	14	2	1701	2019
3	15	2	-2867	-3369
3	16	2	2933	3421
4	0	2	2773	3219
4	1	2	-2773	-2291
4	3	2	-2261	-2394
4	6	2	9997	10056
4	14	2	5896	6193
5	1	2	3659	3854
5	2	2	-3659	-3912
5	3	2	-3296	-3400
5	5	2	-2867	-3708
5	6	2	5175	5436
5	7	2	11443	12960
5	8	2	-4937	-4950
5	11	2	-3559	-3503
5	12	2	4265	4401
5	13	2	6457	7499
5	14	2	-2960	-2761
6	0	2	2307	2469
6	4	2	2820	3240
6	7	2	3753	3302
6	10	2	7341	7785
6	13	2	-1934	-2378
7	1	2	-3100	-2640
7	2	2	5127	5731
7	3	2	7504	8049
7	4	2	-2121	-2502
7	7	2	-2355	-2639
7	8	2	2215	2568
7	9	2	1678	1994
7	11	2	3799	4324
8	0	2	7831	9192
8	3	2	4638	4576
8	4	2	1341	2022
8	5	2	-2820	-2847
8	9	2	3171	3128
9	1	2	2447	3063
9	2	2	-2634	-3180
9	3	2	1469	1438
9	4	2	1375	1673
9	5	2	-1292	-1211
9	6	2	3076	3982

electron density projection on to (001), containing only the terms $h+k=2n$, verified all the metal positions and showed that an additional metal atom was at $(0,\frac{1}{2})$. The interpretation of the forthcoming oxygen structure was complicated by the doubling of each oxygen peak by reproduction across the pseudo-centre at $(\frac{1}{4},\frac{1}{4})$. Guided, however, by their spatial arrangement around the metals, we were able to fix the oxygen positions by choosing an appropriate set of peaks for each half of the asymmetric unit, and thereby restoring the correct symmetry.

With the oxygen structure interpreted in this manner, it became apparent that the metal at (0·28, 0·36) was tetrahedrally coordinated. Taken into consideration with the smaller size of its peak when another F_{hk0} projection was computed, this seemed most likely to be an aluminum atom, while its counterpart across the pseudo-centre was octahedral titanium. From the size of their electron density peaks, the atoms at (0,0) and (0,0·29) were also aluminum, both octahedrally coordinated, so that the remaining atom appearing at $(0,\frac{1}{2})$ was necessarily sodium, thus satisfying a formula $NaTi_2Al_5O_{12}$ for the compound.

Electron density projections on to (001) were used to refine this structure (Fig. 2) and continued with a number of least-squares cycles with the two-dimensional data, using isotropic temperature factors for each atom, until R dropped to 8·7%. The weighting scheme of Cruickshank, Pilling, Bujosa, Lovell & Truter (1961) was adopted, and the matrix inversion involved the block-diagonal approximation.

At this stage the $hk1$ and $hk2$ data were included, it being assumed that the atoms were situated on the mirror planes at $z=0$ and $\frac{1}{2}$ of the space group *Pbam*, one aluminum at the origin in 2(*a*), sodium at 2(*d*) and each of the remaining atoms in either of 4(*h*) or 4(*g*). The isotropic temperature factor for Na proved to be troublesome, rising to an extremely high value of 8 $Å^{-2}$, with an R value of 12·2%. A three-dimensional electron density section $(0,y,z)$ showed it to be in 2(*d*), but the contours were elongated along the **c** direction.

These two effects could have arisen for a number of reasons. In the first instance the Na might be incorrectly placed in its octahedral environment, and indeed it is possible to give it an alternative tetrahedral position by assigning it to the 2(*b*) position of *Pba*2, *i.e.* at $0\frac{1}{2}z$, $\frac{1}{2}0z$ with $z=\frac{1}{4}$. Sodium has this configuration in the two isostructural compounds β-$NaFeO_2$ (Bertaut & Blum, 1954) and $NaAlO_2$ (Théry, Lejus, Briançon & Collongues, 1961). This reduction of symmetry group freed all the atoms from the mirror planes perpendicular to the *c* axis, and a number of least-squares refinement cycles, including anisotropic thermal factors, moved them all appreciably. Not only did the internuclear distances become unrealistic but the temperature factor for Na worsened, and consequently this model was abandoned.

A second possibility is to retain the space group *Pbam* and assume that the two Na atoms in the unit cell statistically occupy the eightfold positions x,y,z, with $x=0$, $y=\frac{1}{2}$, $z=\frac{1}{4}$. This places one half Na in each of $0,\frac{1}{2},\frac{1}{4}$; $0,\frac{1}{2},\frac{3}{4}$; $\frac{1}{2},0,\frac{3}{4}$. Local ordering can now be imagined, with Na occupying one position, $0,\frac{1}{2},\frac{1}{4}$ in one series of the structural tunnels, whereas it adopts as an alternative either $0,\frac{1}{2},\frac{3}{4}$ or $\frac{1}{2},0,\frac{3}{4}$ in the next unit cell or in the symmetry-related equivalent position. Despite the plausibility of this model, which is supported by evidence from a number of related systems

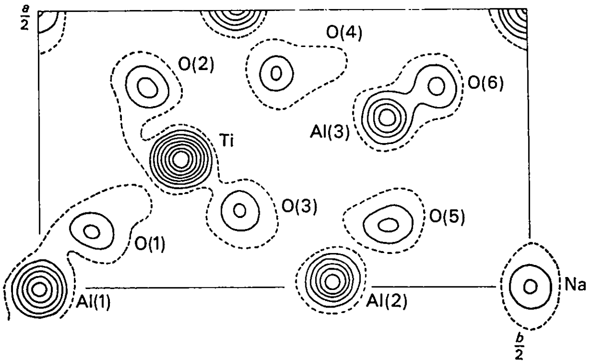

Fig. 2. Electron density projection on to (001), contoured at intervals of three electrons, with zero dotted.

Table 4. *Fractional atomic coordinates and thermal parameters*

E.s.d.'s are given in brackets.

	Space group *Pbam* (no. 52)				Mean-square-amplitude tensors					
	Point position	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
Na	2(*d*)	0	$\frac{1}{2}$	$\frac{1}{2}$	0·052 (20)	0·038 (23)	0·129 (25)	−0·002 (25)	0	0
Al(1)	2(*a*)	0	0	0	0·005 (5)	0·012 (5)	0·003 (9)	−0·005 (9)	0	0
Al(2)	4(*g*)	0·0098 (9)	0·2999 (5)	0	0·011 (5)	0·016 (6)	0·017 (9)	−0·006 (10)	0	0
Al(3)	4(*h*)	0·3069 (9)	0·3553 (7)	$\frac{1}{2}$	0·005 (8)	0·004 (7)	0·024 (13)	0·004 (12)	0	0
Ti	4(*h*)	0·2294 (6)	0·1449 (4)	$\frac{1}{2}$	0·016 (3)	0·019 (4)	0·020 (6)	−0·005 (7)	0	0
O(1)	4(*h*)	0·1050 (19)	0·0513 (13)	$\frac{1}{2}$	0·005 (12)	0·009 (14)	0·025 (20)	−0·019 (21)	0	0
O(2)	4(*g*)	0·3638 (20)	0·1108 (14)	0	0·012 (13)	0·016 (14)	0·025 (19)	−0·010 (24)	0	0
O(3)	4(*g*)	0·1319 (22)	0·2059 (14)	0	0·019 (14)	0·027 (17)	0·008 (23)	−0·036 (24)	0	0
O(4)	4(*h*)	0·3902 (24)	0·2481 (14)	$\frac{1}{2}$	0·016 (14)	0·014 (16)	0·035 (24)	−0·011 (20)	0	0
O(5)	4(*h*)	0·1100 (22)	0·3534 (16)	$\frac{1}{2}$	0·027 (15)	0·026 (18)	0·032 (24)	0·005 (30)	0	0
O(6)	4(*g*)	0·3662 (21)	0·4072 (14)	0	0·016 (14)	0·027 (16)	0·025 (21)	0·002 (26)	0	0

(Wadsley, 1964), the temperature factor for Na did not improve.

A third possibility is the fractional occupancy by Na of the positions available to it. If there is less than the stoichiometric amount of Na, the composition would be balanced by replacing a fraction of the octahedral Al by Ti according to the formula $Na_{1-x}Ti_2(Al_{5-x}Ti_x)O_{12}$. This would be reflected in the temperature factors of these atoms, which appear, however, to be normal.

Finally the temperature effects might be real. Several least-squares cycles, run with anisotropic temperature factors, soon reached a steady state, U_{33} for Na being the only anomaly. The final R value for the observed data was 9·7%. The positional and thermal parameters are listed in Table 4 and the bond lengths in Table 5. Reliance on interatomic distances in specific directions to an accuracy better than the component $(U_{ij})^{\frac{1}{2}}$ cannot be claimed, and the standard deviations of the Na–O bonds in Table 5 are very much underestimated.

The decision between partial occupancy, distribution statistics or large amplitudes of thermal motion is extremely difficult to make unambiguously by crystallographic methods alone. This dilemma has also arisen in a number of additional mixed metal oxides containing alkali, trivalent and quadrivalent metals that we are currently studying, and the structure of a new high-temperature non-stoichiometric phase $Na_xFe_xTi_{2-x}$ ($0·90 > x > 0·75$) is relevant to the present case. Here one component of the anisotropic thermal corrections for Na is also very large, which once again corresponds to the direction of elongation of the open tunnels in which these ions are sited (Mumme & Reid, 1967). We believe that this oscillation of Na is permitted by its freedom to move relatively unhindered within the tunnels created by the rigid framework, an effect which may prove to be a general feature for this class of compound.

Description

The structure is illustrated by Figs. 3 and 4. There are four crystallographically non-identical octahedral sites, two aluminum, one titanium and one sodium, as well as one tetrahedral aluminum. The six Ti–O bonds vary between 1·84 and 2·17 Å (Table 5) which is normal. The octahedral Al(2)–O distances range from 1·83 to 1·97 Å. These two atoms with their ligands constitute the backbone of the structure, forming a double string by edge-sharing and elongated along the z direction,

Table 5. *Interatomic distances and e.s.d.'s* (Å)

Al(1)–O(1)	1·915 ± 0·015 (4)	Al(2)–O(3)	1·830 ± 0·018 (1)	Al(3)–O(6)	1·750 ± 0·019 (2)	Ti—O(1)	1·843 ± 0·016 (1)
Al(1)–O(6′)	1·885 ± 0·018 (2)	Al(2)–O(2′)	1·916 ± 0·018 (1)	Al(3)–O(5)	1·790 ± 0·021 (1)	Ti—O(4)	2·167 ± 0·019 (1)
O(1) –O(1′)	2·48 ± 0·02 (2)	Al(2)–O(5)	1·910 ± 0·020 (2)	Al(3)–O(4)	1·827 ± 0·020 (1)	Ti—O(2)	1·973 ± 0·017 (2)
O(1) –O(6′)	2·68 ± 0·02 (4)	Al(2)–O(4′)	1·966 ± 0·019 (2)	O(4) –O(5)	3·03 ± 0·03 (1)	Ti—O(3)	1·952 ± 0·018 (2)
O(1) –O(6″)	2·69 ± 0·02 (4)	O(5) –O(4′)	2·55 ± 0·03 (2)	O(5) –O(6)	2·87 ± 0·03 (1)	O(2)–O(3)	2·57 ± 0·02 (2)
O(1) –O(1″)	2·91	O(3) –O(5)	2·72 ± 0·03 (2)	O(4) –O(6)	2·87 ± 0·03 (1)	O(2)–O(4)	2·59 ± 0·03 (2)
		O(3) –O(4′)	2·73 ± 0·03 (2)	O(6) –O(6′)	2·91	O(1)–O(2)	2·92 ± 0·02 (2)
Na—O(2)	2·57 ± 0·02 (4)	O(2′)–O(5)	2·73 ± 0·03 (2)			O(1)–O(3)	2·82 ± 0·02 (2)
Na—O(5)	2·49 ± 0·02 (2)	O(2′)–O(4′)	2·59 ± 0·02 (2)			O(3)–O(4)	2·84 ± 0·03 (2)
O(2) –O(2′)	4·24 ± 0·03 (2)	O(4) –O(4)	2·91			O(3)–O(3)	2·91
O(5) –O(2)	2·73 ± 0·02 (4)	O(5) –O(5)	2·91			O(2)–O(2)	2·91
O(5) –O(2′)	4·26 ± 0·03 (4)						
O(2) –O(2)	2·91 (2)						

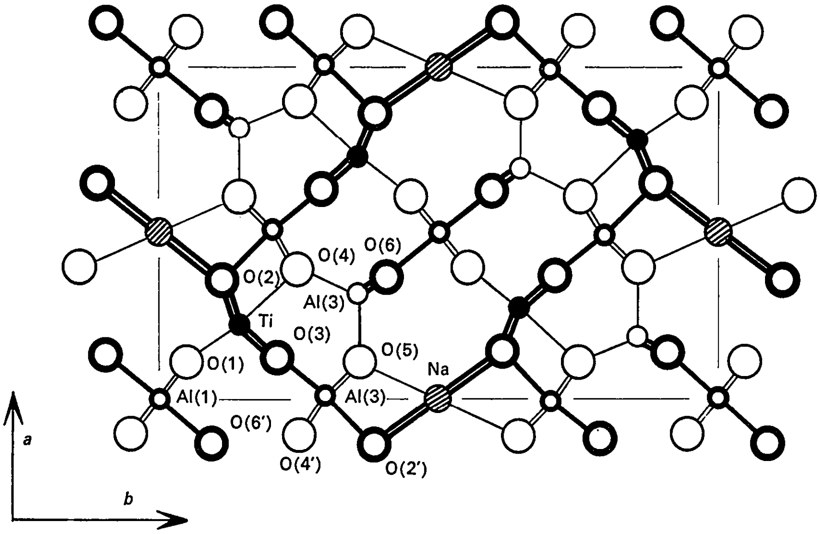

Fig. 3. Structure of $NaTi_2Al_5O_{12}$. Al(1), Al(2), O(2), O(3) and O(6) and their symmetry related equivalents are at $z=0$, while Na, Al(3), Ti, O(1), O(4) and O(5) are all at $z=\frac{1}{2}$.

one string containing Ti, the other Al(2). They are represented by line shading in Fig. 4. The double groups join by common corners to form stepped sheets normal to the *b* axis, and adjacent sheets are staggered relative to each other. Union between them is effected by the third octahedron centred about Al(1) (stippled in Fig. 4) sharing corners with those centred about Ti from two different sheets. In cross-section each octahedron containing either Ti or Al is joined to others centred about metal atoms of the other kind. Al(3) is tetrahedrally coordinated, and the bond distances to oxygen of 1·75, 1·79 and 1·83 Å are normal (*International Tables for X-ray Crystallography*, 1962, p. 262). The nearest neighbour metal atoms to it are all aluminum. This arrangement leaves a series of irregular holes, which as we have already discussed in some detail, accommodate Na in an octahedral environment. This is very similar to the one it adopts in rhombohedral α-$NaFeO_2$ (Goldsztaub, 1935).

Although this unusual structure has no close overall similarities to any known types, the double strings appear in a wide variety of oxides containing the transition metals. Particularly noteworthy are their presence in two aluminum compounds, AlOOH (diaspore; Deflandre, 1932) and θ-Al_2O_3 which is isomorphous with β-Ga_2O_3 (Geller, 1960). In the former the double strings form open tunnels which presumably enclose the protons, whereas in the latter they are joined through tetrahedrally coordinated ions.

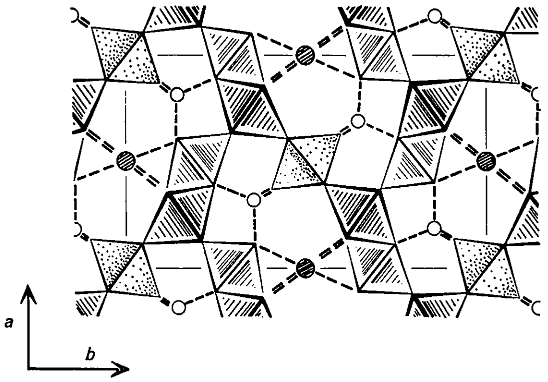

Fig. 4. $NaTi_2Al_5O_{12}$ showing the double octahedral strings in cross-section, the more heavily shaded ones being Ti, the lighter Al. These are bridged by the stippled octahedra enclosing Al, while the larger hatched circles are Na and the smaller are tetrahedral Al.

The presence of these two coordination polyhedra in $NaTi_2Al_5O_{12}$, together with the presence of both tri- and quadri-valent elements, suggested to us that it might be the progenitor of a family of isomorphous phases formed by ionic substitution. The replacement of Al by Fe^{3+} could lead to magnetically interesting compounds; for example $NaTi_2Fe_5O_{12}$ might be expected to have Fe in two different coordination modes, while in $NaGe_2Fe_5O_{12}$ the Ge could be confined to the tetrahedra with all the Fe octahedral. Attempts to synthesize these compounds by a variety of techniques, however, have so far proved unsuccessful.

References

Andersson, S. & Wadsley, A. D. (1962*a*). *Acta Cryst.* **15**, 194.

Andersson, S. & Wadsley, A. D. (1962*b*). *Acta Cryst.* **15**, 201.

Bayer, G. & Hoffmann, W. (1965). *Z. Kristallogr.* **121**, 9.

Bertaut, F. & Blum, P. (1954). *C.r. Acad. Sci. Paris*, **239**, 429.

Cruickshank, D. W. J., Pilling, D. E., Bujosa, A., Lovell, F. M. & Truter, M. R. (1961). In *Computing Methods and the Phase Problem in X-ray Crystal Analysis*, p. 32. Oxford: Pergamon Press.

Daly, J. J., Stephens, F. S. & Wheatley, P. J. (1963). Monsanto Research S.A., Final Report no. 52.

Deflandre, M. (1932). *Bull. Soc. franç. Minér. Crist.* **55**, 140.

Geller, S. (1960). *J. Chem. Phys.* **33**, 676.

Goldsztaub, S. (1935). *Bull. Soc. franç. Minér. Crist.* **58**, 6.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

Mumme, W. G. & Reid, A. F. (1967). *Acta Cryst.* Submitted for publication.

Théry, J., Lejus, A. M., Briançon, D. & Collongues, R. (1961). *Bull. Soc. chim. Fr.* p. 973.

Wadsley, A. D. (1964). In *Non-Stoichiometric Compounds*, edited by L. Mandelcorn, p. 111 *et seq.* New York: Academic Press.