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The Structure of $Na_4Mn_4Ti_5O_{18}$

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$Na_4Mn_4Ti_5O_{18}$, formed at 1200 °C by crystallization from the composition $NaMnTiO_4$, is orthorhombic, with unit-cell dimensions $a = 9\cdot268$, $b = 26\cdot601$, $c = 2\cdot888$ Å. Mn^{3+} and Ti^{4+} atoms occupy octahedral positions, while the coordination of another Mn^{3+} is a rectangular pyramid. In this structure, groups of octahedra, joined by extensive edge and corner sharing, are linked together by the five-coordinated Mn^{3+} to leave a series of tunnels for the sodium ions. One of these is a single tunnel similar to that found in calcium ferrite; the other is a much larger one and contains sites for four sodium ions, only half of which are filled. The chemical composition was deduced from this structure analysis.

Introduction

An investigation of a group of alkali-transition metal oxides of the form $NaA^{3+}B^{4+}O_4$ (Reid, Wadsley & Sienko, 1967) has shown that many of them, including $NaScTiO_4$, $NaScZrO_4$, $NaScHfO_4$, $NaFeSnO_4$, $NaScSnO_4$ and $NaFeTiO_4$ prepared below their melting points, are isomorphous with calcium ferrite. Another compound close to these in overall stoichiometry, $Na_{0\cdot9}Fe_{0\cdot9}Ti_{1\cdot1}O_4$, formed a related structure, the outstanding features of which were greater edge sharing of the octahedra, and the formation of double tunnels to accommodate the sodium atoms (Mumme & Reid, 1968).

Attempts to make additional compounds isomorphous with these were unsuccessful. '$NaAlTiO_4$' formed $Na_2Ti_7O_{15}$ together with other unidentified phases (Wadsley & Mumme, 1968) while '$NaCoTiO_4$' and '$NaNiTiO_4$' each formed a number of heteropolytypes containing more or less sodium, and having layer struc-

tures with close similarities to α-$NaFeO_2$ (Mumme, Reid & Wadsley, 1968). In all of these there were obvious and gross changes of composition. $NaMnTiO_4$, however, prepared by solid state reaction appeared to form a unique congruently melting single phase. The ideal composition of it, $Na_4Mn_4Ti_5O_{18}$, was derived from this structural analysis.

Experimental

Well formed prismatic crystals of $Na_4Mn_4Ti_5O_{18}$ were originally prepared by melting the composition '$NaMnTiO_4$' at 1200 °C. The weight loss from 5 grams of sample, a mixture of TiO_2, sodium oxalate and MnO_2 held in a platinum dish, was only 0·3% greater than the expected weight loss for total conversion of Mn^{4+} to Mn^{3+}.

The approximate lattice parameters were determined from single-crystal photographs and were used to index the powder diffractometer data, which had been col-

lected with potassium chloride as an internal standard. By using least-squares refinement and index selection programs to determine the final parameters and indices, it was possible to index all but one weak line of the first thirty one. These powder data are given in Table 1 and the crystallographic constants in Table 2.

Table 1. *Powder diffractometer data*

I (obs)	$\sin^2 \theta$ (obs)	$\sin^2 \theta$ (calc)	h	k	l
m	0·00326	0·00335	0	2	0
m	0·00762	0·00775	1	1	0
m	0·01331	0·01341	0	4	0
m	0·01433	0·01445	1	3	0
s	0·02022	0·02032	1	4	0
s	0·02759	0·02787 }	1	5	0 }
		0·02763 }	2	0	0 }
s	0·02834	0·02847	2	1	0
w	0·03499	0·03517	2	3	0
m	0·03694	0·03709	1	6	0
w	0·05358	0·05366	0	8	0
w	0·07548	0·07558	3	4	0
s	0·08301	0·08312	3	5	0
s	0·08359	0·08384	0	10	0
m	0·09227	0·09235	3	6	0
s	0·09884	0·09900 }	1	5	1 }
		0·09876 }	2	0	1 }
m	0·10830	0·10822 }	1	6	1 }
		0·10836 }	1	11	0 }
w	0·12456	0·12479	0	8	1
w	0·13172	0·13170 }	1	8	1 }
		0·13147 }	4	5	0 }
m	0·13403	0·13413	3	1	1
w	0·13647	0·13665	3	2	1
m	0·14595	0·14595	1	9	1
m	0·16667	0·16667	2	9	1
ms	0·18136	0·18165	4	0	1
ms	0·18250	0·18260	2	10	1
m	0·25071	0·25081	3	15	0
mw	0·25760	0·25722	2	4	1
ms	0·26588	0·26549	4	10	1
ms	0·26704	0·26669	1	15	1
m	0·28459	0·28453	0	0	2
mw	0·36790	0·36765	3	5	2

Table 2. *Crystallographic data for* $Na_4Mn_4Ti_5O_{18}$

Symmetry	Orthorhombic
Unit-cell dimensions	$a = 9\cdot268 \pm 0\cdot005$ Å
	$b = 26\cdot601 \pm 0\cdot005$
	$c = 2\cdot888 \pm 0\cdot002$
Systematically absent reflexions	$0kl \quad k \neq 2n$
	$h0l \quad h \neq 2n$
Possible space groups	$Pba2$ (No. 32)
	$Pbam$ (No. 55)

$$D_x = 3\cdot91 \text{ g.cm}^{-3}$$
$$D_m = 4\cdot06 \pm 0\cdot15 \text{ g.cm}^{-3}$$
$$Z = 2$$
$$\mu_c = 115 \text{ cm}^{-1}$$

Intensity data hkl for the levels $l = 0$, 1 and 2 were obtained from a crystal measuring $0\cdot1 \times 0\cdot02 \times 0\cdot02$ mm by the integrated Weissenberg technique with the use of filtered copper radiation. Corrections for absorption were found to be unnecessary, as μR is $0\cdot12$.

Intensities were measured visually with a standard scale, and the reduction to structure amplitudes, and all subsequent computing was made on the Division's Elliott 803 computer with 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 the ionized atoms Na^+, Mn^{3+}, Ti^{4+} were taken from *International Tables for X-ray Crystallography* (1962, p.201 *et seq.*). The scattering curve for O^{2-} was that of Suzuki (1960).

Determination of the structure

A feature of the c-axis Weissenberg photographs is that the intensity distribution in the zero level is virtually identical with that in the second level. This allows no positions other than those at $z = 0$ and $\frac{1}{2}$ for every atom in the unit cell, and the space group becomes *Pbam* rather than *Pba2*, with the atoms in the fourfold positions $2(d)$, $2(c)$, $2(b)$ or $2(a)$.

A pycnometric determination of the density gave a value of $D_m = 4\cdot06 \pm 0\cdot15$ g.cm^{-3} from which the number of formula units was calculated to be $9\cdot2$. However the fact that all but one of the powder reflexions had been indexed with the use of the unit-cell dimensions obtained from the single-crystal determination indicated the formation of the single phase $NaMnTiO_4$, and the above result could be rationalized only by assuming the measured density to be too low and that the value of Z was 10. Only after the structure had been solved and the composition determined uniquely as $Na_4Mn_4Ti_5O_{18}$ and with $Z = 2$ did it become apparent that the measured density although slightly high was in accord with the structure.

Since the length of the c axis is only $2\cdot888$ Å all the atoms should be clearly resolved in the (001) projection, and for this reason the structure determination initially was confined to the $hk0$ level. The sharpened Patterson function $P(uv)$, shown in Fig. 1, indicated considerable overlap of the vectors between atoms possessing a strong pseudo-hexagonal arrangement.

In this Figure there were only two strong vectors with lengths close to the metal–metal distance for a pair of edge-shared octahedra. Even so both were rather long, $3\cdot0$ and $3\cdot2$ Å, compared with the more usual values of $2\cdot8$ Å for projections of the present kind. Since it was anticipated that the structure was made up of a network of edge-shared octahedra, it was concluded that these groups, if they existed, would be aligned along the [530] direction as defined by the shorter of these two vectors.

With $Na_{10}Mn_{10}Ti_{10}O_{40}$ as the assumed contents of the unit cell it was necessary to have the Mn and Ti atoms randomly occupying five fourfold positions, and the oxygen atoms in another ten fourfold positions.

Table 3. *Observed and calculated structure factors*

H	K	L	F$_o$	F$_c$

The ten sodium atoms would necessarily occupy two fourfold and one twofold position, and the latter could be taken as the origin. The only suitable environment for this sodium atom which would satisfy the conditions of symmetry imposed by the space group seemed to be the one it has in the hollandite structure (Byström & Byström, 1950) and furthermore, the pairs of octahedra in such an arrangement were aligned in the direction deduced from the Patterson function. Attempts to create models with this fragment of the structure at the origin did not lead to any satisfactory solution.

At this stage is seemed clear that unless the positions of some of the metal atoms could be fixed, the structure would be difficult to solve using only the information contained in the Patterson projection. Unitary structure factors for 73 of the zero-level reflexions were calculated, 32 of which had values of $U > 1.5$, and by systematic application of the sign relation $S(h)S(h+h') \approx S(h)$, using the method described by Grant, Howells & Rogers (1957), a self consistent set of signs was deduced for 17 of them. A two-dimensional Fourier synthesis $\varrho(xy)$ based on the signs of these reflexions suggested that the metal atoms occupied the same positions as the strong peaks in the Patterson. No logical oxygen structure was forthcoming but it did seem that the atom at the origin was Ti or Mn rather than a lighter sodium. This was not possible with the formula NaMnTiO$_4$, but if it was conceded that there were only 8 sodium atoms in the unit cell, an octahedral metal placed at the origin would satisfy the space group criteria.

Structure factors were calculated for a model which contained atoms of average manganese and titanium scattering power at $(\frac{1}{2},0)$, $(\frac{1}{3},1/10)$, $(0,1/10)$, $(\frac{1}{3},3/10)$ and $(0,3/10)$. In the light of previous experience (Mumme & Wadsley, 1967) a false centre of higher symmetry was avoided by placing sodium atoms in the further two positions $(\frac{1}{6},2/10)$ and $(\frac{1}{6},4/10)$. No atom

was included at $(\frac{1}{4},\frac{1}{4})$, the position of another strong peak in the Patterson projection, for this would bring metal atoms too close together.

A two-dimensional Fourier synthesis onto (001) verified all the metal positions chosen, and this process was repeated with more accurate positions calculated from the previous Fourier syntheses until parts of the oxygen structure became clear. The group of three edge-shared octahedra centred about $(0,\frac{1}{2})$ were first recognized, and successive electron-density projections revealed that this was corner shared to another group of two edge-shared octahedra. The manner in which these two blocks were further joined remained a puzzle until it was realized that the metal at $(0,3/10)$ was Mn^{3+} in fivefold coordination. Electron-density projections onto (001) were continued until in the last stages (Fig. 2) it was possible to recognize a smaller peak at $(\frac{1}{3},\frac{1}{2})$ as another sodium atom, now leaving only two alternatives of composition Na$_5$Mn$_5$Ti$_4$O$_{18}$ or Na$_4$Mn$_4$Ti$_5$O$_{18}$. Both of these were investigated by a number of least-squares refinement cycles with the two-dimensional data, including isotropic temperature factors for each atom as variables. The weighting scheme of Cruickshank, Pilling, Bujosa, Lovell & Truter (1961) was adopted, and the matrix inversion involved the block diagonal approximation.

For Na$_5$Mn$_5$Ti$_4$O$_{18}$ with Mn^{3+} atoms at $(0,3/10)$, $(\frac{1}{3},1/10)$ and $(\frac{1}{2},0)$ the R value dropped to 10·3%, but the temperature factor for the sodium atom at $(\frac{1}{6},4/10)$ increased to the high value of 7 Å^2 which indicated the possibility that this site as well as that at $(\frac{1}{3},\frac{1}{2})$, was not fully occupied. In this case the formula is incorrect, as this position must be completely filled. On the other hand, Na$_4$Mn$_4$Ti$_5$O$_{18}$ with Mn^{3+} at $(0,3/10)$ and $(\frac{1}{3},1/10)$, and with Na$(\frac{1}{6},4/10)$ and Na$(\frac{1}{3},\frac{1}{2})$ half occupied refined until R became 9·7%, and furthermore all temperature factors behaved normally. The final temperature factors of the metal atoms for both of these cases are compared in Table 4. It should be borne in mind, however, that the possible presence of extinction could have some effect on all of these temperature factors.
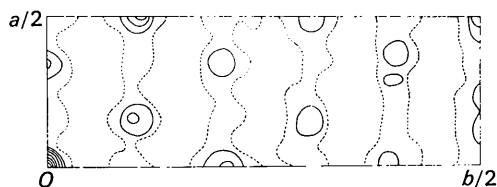

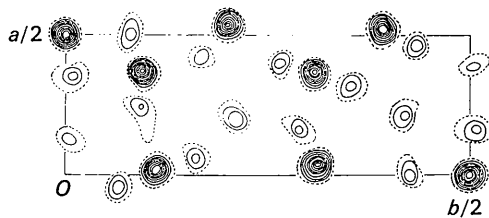Fig. 1. Patterson function $P(uv)$ projected onto (001).

Fig. 2. Electron density projections onto (001). The contours are at arbitrary intervals.

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Table 4. *Thermal parameters for the preferred and alternative composition, calculated from the two-dimensional data for the structural models*

1. Na$_4$Mn$_4$Ti$_5$O$_{18}$*		2. Na$_5$Mn$_5$Ti$_4$O$_{18}$	
Atom	B	Atom	B
Na(1)	2·4 (0·6) Å^2	Na(1)	2·4 (0·6) Å^2
$\frac{1}{2}$Na(2)	1·0 (0·7)	Na(2)	6·9 (1·0)
$\frac{1}{2}$Na(3)	0·5 (0·7)	$\frac{1}{2}$Na(3)	0·6 (0·8)
Mn(1)	1·5 (0·2)	Mn(1)	1·4 (0·2)
Mn(2)	0·9 (0·2)	Mn(2)	0·8 (0·2)
Ti(1)	0·4 (0·3)	Mn(3)	1·1 (0·2)
Ti(2)	0·3 (0·2)	Ti(1)	0·2 (0·2)
Ti(3)	0·3 (0·2)	Ti(2)	0·2 (0·2)

* Model 1, that accepted, required half occupancy for Na(2) and Na(3) and gave $R=9·7$. In model 2, Mn(3) replaced Ti(1), giving $R=10·3$.

This structural model for $Na_4Mn_4Ti_5O_{18}$ therefore exhibited a chemical composition close to $NaMnTiO_4$, a low residual for the structure factors, more normal behaviour of the temperature factors during refinement, and furthermore the octahedral Mn^{3+} atom possessed the one long oxygen ligand of 2·3 Å, distinguishing it from the other octahedral sites occupied by Ti^{4+}. All of these features were taken as collective criteria for the validity of this model and further possibilities such as having one Mn^{3+} atom randomly distributed throughout all the octahedral sites were not merited and were not investigated.

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 titanium atom in $2(c)$ and each of the remaining atoms in either $4(h)$ or $4(g)$. Refinement proceeded normally to give the final R value of 12·34%. No attempt was made to refine further by using anisotropic temperature factors as variables, nor was refinement attempted using the alternative space group $Pba2$.

The positional and thermal parameters with their standard deviations are listed in Table 5 and the bond lengths in Table 6.

Table 5. *Fractional atomic coordinates and thermal parameters space group Pnam (No. 55)*

	Point position	x	y	z	B
Ti(1)	2(c)	0·0	$\frac{1}{2}$	0	0·7 (0·1) Å²
Ti(2)	4(h)	0·3572 (6)	0·3061 (2)	$\frac{1}{2}$	1·0 (0·1)
Ti(3)	4(g)	0·0142 (6)	0·1081 (2)	0	0·8 (0·1)
Mn(1)	4(g)	0·0314 (7)	0·3066 (2)	0	2·1 (0·1)
Mn(2)	4(h)	0·3618 (5)	0·0903 (2)	$\frac{1}{2}$	1·5 (0·1)
Na(1)	4(g)	0·2077 (17)	0·2051 (5)	0	2·7 (0·3)
Na(2)	4(h)	0·2064 (26)	0·4155 (8)	$\frac{1}{2}$	1·5 (0·4)
Na(3)	4(g)	0·1269 (38)	0·0051 (12)	0	3·4 (0·6)
O(1)	4(g)	0·3631 (25)	0·0049 (8)	$\frac{1}{2}$	1·8 (0·4)
O(2)	4(h)	0·2223 (23)	0·0933 (7)	0	1·3 (0·4)
O(3)	4(g)	0·0496 (23)	0·1610 (7)	$\frac{1}{2}$	1·4 (0·4)
O(4)	4(g)	0·4181 (25)	0·1641 (8)	$\frac{1}{2}$	1·7 (0·4)
O(5)	4(g)	0·1621 (23)	0·2833 (8)	$\frac{1}{2}$	1·4 (0·4)
O(6)	4(h)	0·4100 (22)	0·2632 (7)	0	1·0 (0·3)
O(7)	4(h)	0·3150 (22)	0·3562 (7)	0	1·0 (0·3)
O(8)	4(h)	0·4999 (21)	0·0754 (7)	0	1·1 (0·3)
O(9)	4(g)	0·4688 (21)	0·4354 (6)	$\frac{1}{2}$	0·7 (0·3)

Table 6. *Interatomic distances and e.s.d.'s*

4 × Ti(1)—O(1)	1·927 ± 0·019
2 × Ti(1)—O(8)	2·007 ± 0·015
4 × O(8) —O(1)	2·69 ± 0·02
4 × O(8′) —O(1′)	2·69 ± 0·02
2 × O(1) —O(1′)	2·55 ± 0·03
2 × O(1) —O(1″)	2·888
1 × Ti(2)—O(5)	1·907 ± 0·017 Å
1 × Ti(2)—O(3′)	1·997 ± 0·017
2 × Ti(2)—O(6)	1·906 ± 0·016
2 × Ti(2)—O(7)	2·003 ± 0·016
2 × O(6) —O(3′)	2·816 ± 0·023
2 × O(7) —O(3′)	2·646 ± 0·023
2 × O(5) —O(6)	2·77 ± 0·02
2 × O(5) —O(7)	2·80 ± 0·02
2 × O(6) —O(7)	2·63 ± 0·02
1 × O(6) —O(6′)	2·888
1 × O(7) —O(7′)	2·888

Table 6 (*cont.*)

1 × Ti(3)—O(2)	1·969 ± 0·017
1 × Ti(3)—O(7′)	2·076 ± 0·016
2 × Ti(3)—O(3)	2·026 ± 0·017
2 × Ti(3)—O(9′)	1·899 ± 0·015
2 × O(2) —O(9′)	2·86 ± 0·02
2 × O(2) —O(3)	2·79 ± 0·02
2 × O(9′)—O(7′)	2·93 ± 0·02
2 × O(3) —O(7′)	2·65 ± 0·02
2 × O(3) —O(9′)	2·65 ± 0·02
1 × O(9′)—O(9″)	2·888
1 × O(3) —O(3′)	2·888
1 × Mn(1)-O(6′)	2·171 ± 0·016
2 × Mn(1)-O(5)	1·985 ± 0·018
2 × Mn(1)-O(4′)	1·948 ± 0·018
2 × O(5) —O(6′)	3·10 ± 0·02
2 × O(4′)—O(6′)	3·00 ± 0·02
2 × O(4′)—O(5)	2·66 ± 0·02
1 × O(5) —O(5′)	2·888
1 × O(4′)—O(4″)	2·888
1 × Mn(2)-O(1)	2·273 ± 0·019
1 × Mn(2)-O(4)	2·032 ± 0·018
2 × Mn(2)-O(8)	1·970 ± 0·016
2 × Mn(2)-O(2)	1·940 ± 0·017
2 × O(1) —O(8)	2·69 ± 0·02
2 × O(1) —O(2)	3·05 ± 0·02
2 × O(8) —O(4)	2·87 ± 0·02
2 × O(2) —O(4)	2·99 ± 0·02
2 × O(8) —O(2)	2·62 ± 0·02
1 × O(8) —O(8′)	2·888
1 × O(2) —O(2′)	2·888
2 × Na(1) -O(3)	2·38 ± 0·02
2 × Na(1) -O(4)	2·66 ± 0·02
1 × Na(1) -O(6)	2·43 ± 0·02
1 × Na(1) -O(2)	2·98 ± 0·02
2 × Na(1) -O(5)	2·57 ± 0·02
1 × Na(1) -O(6′)	2·98 ± 0·02
1 × O(4) —O(4′)	2·888
1 × O(5) —O(5′)	2·888
1 × O(3) —O(3′)	2·888
2 × Na(2) -O(7)	2·36 ± 0·02
1 × Na(2) -O(9)	2·49 ± 0·02
1 × Na(2) -O(1′)	2·21 ± 0·03
2 × Na(2) -O(8′)	2·41 ± 0·02
1 × O(8′)—O(7)	3·44 ± 0·02
1 × O(9) —O(1′)	3·46 ± 0·02
1 × O(9′)—O(1″)	3·46 ± 0·02
2 × Na(3) -O(9″)	2·51 ± 0·03
2 × Na(3) -O(1)	2·62 ± 0·03
1 × Na(3) -O(2)	2·51 ± 0·03
2 × Na(3) -O(9′)	2·60 ± 0·03
1 × O(9″)—O(9‴)	2·888
1 × O(9′)—O(9″)	2·888
1 × O(1) —O(1′)	2·888

Description

The structure is illustrated by Fig.3(a) and (b). There are four crystallographically non-identical octahedra forming blocks by edge-sharing which are further joined by corner-sharing into groups of seven. The two double and one triple blocks make up a group which is then linked to each adjacent block through five-coordinated Mn^{3+}. This arrangement leaves a series of tunnels, of two kinds, which accommodate the sodium atoms.

In one the sodium has a coordination similar to that of Ca^+ in calcium ferrite. Of a total of nine oxygen neighbours, three at $z = \frac{1}{2}$ and three at $z = -\frac{1}{2}$ are located about the central Na atom at the corners of
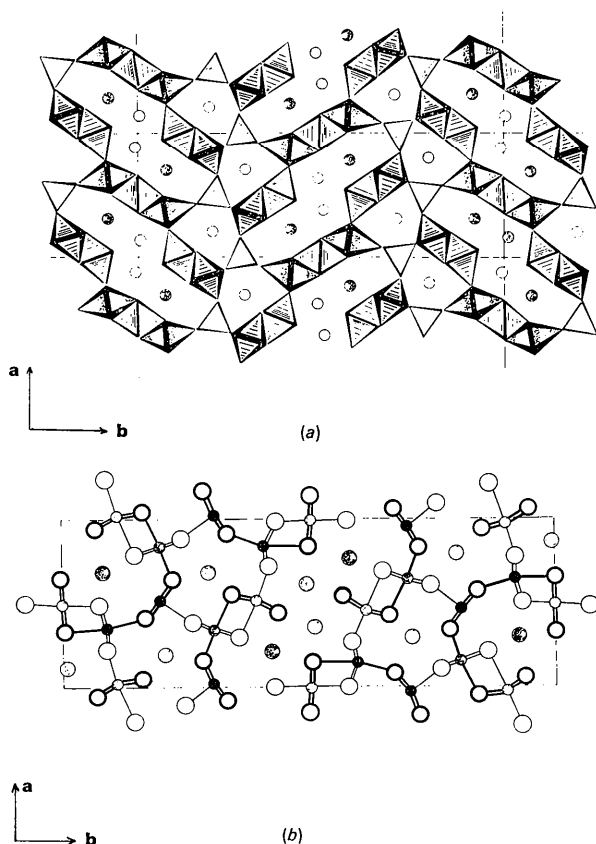

a ↑
└──→ b   (a)

↑a
└──→ b   (b)

Fig. 3. (a) Crystal structure of $Na_4Mn_4Ti_5O_{18}$. Heavy markings are centred at $y = \frac{1}{2}$ and light markings at $y = 0$. Stippled circles are Na atoms. Triangles represent rectangular pyramids containing Mn^{3+} near the basal plane. (b) Crystallographic sites in $Na_4Mn_4Ti_5O_{18}$. Heavy circles show sites at $y = \frac{1}{2}$ and light circles sites at $y = 0$. Small black circles Mn, small stippled circles Ti. Large open circles are oxygen atoms and large stippled circles sodium.
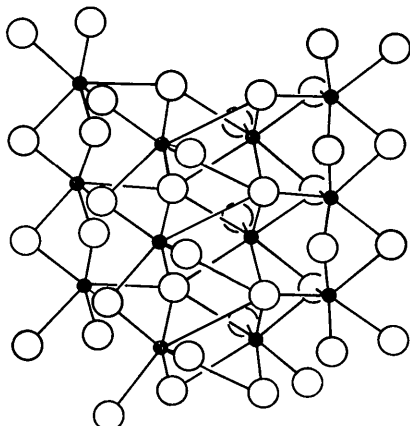

Fig. 4. The Na–O coordination in the large tunnel of Na_4Mn_4–Ti_5O_{18}. Small circles Na, large circles O.

a right triangular prism, while three additional atoms are located out from the three prism faces. There are seven nearest neighbours with Na–O bond distances between 2·38 and 2·66 Å, being the six oxygen atoms at the corners of the triangular prism, and the one out from the largest face. The other two bond lengths are 2·89 and 2·98 Å.

The other type of tunnel is much larger and has an unusual flattened S shape. It contains four sites for sodium atoms, two with sixfold coordination to their nearest oxygen neighbours and two with sevenfold coordination, shown in Fig. 4. Only half of these are occupied however, and probably the atoms in each pair of the crystallographically non-identical sites are absent, in turn, from adjacent unit cells. In any event, the two central atom sites could not possibly be fully occupied in one unit cell as their separation is only 2·2 Å.

Both types of sodium coordination polyhedra which have joined to form this tunnel are basically similar to the one described above. In each the sodium atom is again the central atom of a triangular prism, but only one has an additional oxygen atom out from a face. The way in which these triangular prisms pack together necessitates a change of orientation with respect to one another and is illustrated by Fig. 5. The Na–O bond lengths in this tunnel lie between 2·38 and 2·98 Å.

The Ti–O distances in their metal octahedra vary between 1·90 and 2·07 Å, which is normal for titanates. For the octahedral manganese the five shorter bonds range from 1·94 to 2·03 Å with one additional longer band of 2·27 Å, due perhaps to a marginal Jahn–Teller effect, which helps to identify this atom as Mn^{3+}. The main distinction of course, comes in the structure determination where the final arbiter is the temperature factor of this atom which, together with all other metal atoms, is quite normal. In the case of less than the stoichiometric amount of sodium being present in this compound its composition would possibly be balanced by replacing a fraction of this octahedral Mn^{3+} by Ti^{4+}.

The other Mn^{3+} lies near the centre of the base of a rectangular pyramid of oxygen atoms with five bond lengths between 1·95 and 2·17 Å. There are no additional bonds, as the next potential oxygen ligands are at distances of 2·94 and 3·15 Å.

Discussion

Mn^{3+} has two kinds of coordination in this structure. The octahedral coordination is somewhat similar to that found in Mn_3O_4 and manganates of bivalent metals (Sinha, Sanjana & Biswas, 1957), but is unusual in that distortion due to a presumed Jahn–Teller effect is confined to one Mn–O bond only. The other bond which would usually be expected to lengthen is perhaps stabilized at a normal Mn–O distance by the multiple edge-sharing, as this octahedron occurs in the triple block Mn–Ti–Mn. In the second kind of site Mn^{3+} is contained in a rectangular pyramid of oxygen atoms

with one longer bond to the apical oxygen, again the possible result of a Jahn–Teller effect. This coordination is the same as that described by Quezel-Ambrunaz, Bertaut & Busson (1964) for the Mn^{3+} sites in Mn_2YO_5, except that they suggested the presence of one additional oxygen neighbour.
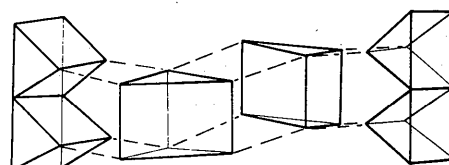
Although the present structure has no close similarity to any other structure type, there are many other examples of 3 Å structures built up from blocks of edge-shared octahedra. Hollandite (Byström & Byström, 1950), calcium ferrite (Hill, Peiser & Rait, 1956) and calcium titanate (Bertaut & Blum, 1956) are examples of structures with double blocks of edge-shared octahedra, while psilomelane (Wadsley, 1953), warwickite and ludwigite (Takeuchi, Watanabe & Ito, 1950), the size increases from two to five. In all of these examples, the blocks are linked by corner sharing to form the different tunnels which characterize these structure types. The structure described here is made up of double and triple blocks, but the difference between it and those mentioned above is that the full linkage of the structure is completed by means of a coordination polyhedron other than an octahedron. This also occurs in Mn_2YO_5 where two single octahedra and three rectangular pyramids make up the basic unit [Fig. 6(a)], and join to form a tunnel typical of the calcium ferrite structure. In $Na_4Mn_4Ti_5O_{18}$ the basic unit is made up of a triple block, two double blocks and two rectangular pyramids [Fig. 6(b)] which are arranged to form a similar tunnel, as well as the much larger S-shaped one. This principle of including a different type of coordination polyhedron may be a useful one for predicting new structures made up fundamentally of blocks of edge-shared octahedra.

The other feature of this structure is the large tunnel which contains the half filled sites for the sodium atoms. While it appears complicated, it too can be broken down into simpler units, the triangular prisms, which pack together as already described. Such units also exist in $Na_{0.9}Fe_{0.9}Ti_{1.1}O_4$ where they join together in pairs to create the double tunnels of that structure.
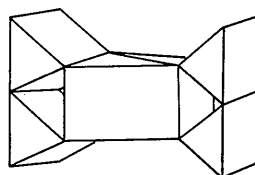
Dr A. F. Reid first prepared this unusual compound and the writer would like to thank both him and Dr A. D. Wadsley for a great amount of help in this investigation.
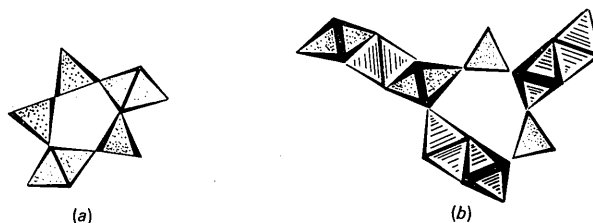

Fig. 5. The disposition of the coordination polyhedra in the large tunnel. (a) is the exploded view of (b) a group of joined polyhedra.

Fig. 6. The basic unit of structure in (a) Mn_2YO_5 and (b) $Na_4Mn_4Ti_5O_{18}$.

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