

# The Crystal Structure of $\text{Na}_2\text{Ti}_3\text{O}_7$

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(Received 20 December 1960 and in revised form 21 March 1961)

The crystal structure of  $\text{Na}_2\text{Ti}_3\text{O}_7$  has been determined, using single-crystal methods. The space group is  $P2_1/m$ , with the unit-cell dimensions

$$a = 8.571, b = 3.804, c = 9.135 \text{ \AA}, \beta = 101.57^\circ.$$

The structure consists of layers of the composition  $(\text{Ti}_3\text{O}_7)^{2-}$ . These are built up from blocks of six  $\text{TiO}_6$  octahedra sharing edges, which are joined by having octahedral corners in common. The layers are held together by sodium ions which occur in two different kinds of crystallographic site.

## Introduction

The alkali metals form a composition series of ternary oxides with titanium dioxide,  $A_2O \cdot n\text{TiO}_2$  ( $1 \leq n \leq 6$ ). We are examining selected members with the object of clarifying the relationships within the system between chemical composition and crystal structure. The dititanate  $\text{K}_2\text{Ti}_2\text{O}_5$  was described recently, (Andersson and Wadsley, 1961), and the structure of the trititanate  $\text{Na}_2\text{Ti}_3\text{O}_7$  is now reported.

## Experimental

$\text{Na}_2\text{CO}_3$  and  $\text{TiO}_2$  (anatase) in the mole ratio 1:2 were heated together at  $1000^\circ\text{C}$  to remove  $\text{CO}_2$  until constant weight was achieved. The crucible was then heated to about  $1300^\circ\text{C}$ . Sodium is evidently lost on fusion, as the clear melt, on cooling, consisted of a single phase with the formula  $\text{Na}_2\text{Ti}_3\text{O}_7$ , a compound previously believed to have an incongruent melting point (Levin and McMurdie, 1959).

Table 1. *Crystallographic Constants for  $\text{Na}_2\text{Ti}_3\text{O}_7$*

Symmetry	Monoclinic
Unit-cell dimensions	$a = 8.571 \pm 0.002 \text{ \AA}$ $b = 3.804 \pm 0.002$ $c = 9.135 \pm 0.002$ $\beta = 101.57^\circ \pm 0.05^\circ$
Systematic absent reflexions	$0k0$ with $k \neq 2n$
Possible space groups	$P2_1, P2_1/m$
	$D_o = 3.40 \pm 0.05, D_c = 3.43 \text{ g.cm.}^{-3}, Z = 2$

The colourless rod-like crystals, of monoclinic symmetry elongated along the  $b$  axis, have the crystallographic constants given in Table 1. These were determined from a Guinier powder pattern (Table 2) internally calibrated with potassium chloride as a standard.

Table 2. *Guinier powder pattern of  $\text{Na}_2\text{Ti}_3\text{O}_7$*

	Cu $K\alpha_1$ radiation		
$I$	$\sin^2 \theta_o$	$hkl$	$\sin^2 \theta_c$
<i>vvw</i>	0.00746	001	0.00741
<i>st</i>	0.00847	100	0.00842
<i>vw</i>	0.01270	101	0.01266
<i>m</i>	0.01968	101	0.01899
<i>vw</i>	0.02972	002	0.02963
<i>vw</i>	0.03478	201	0.03474
<i>st</i>	0.04941	110	0.04941
<i>vvw</i>	0.05055	202	0.05063
<i>w</i>	0.05995	111	0.05999
<i>vw</i>	0.06551	103	0.06559
<i>w</i>	0.06660	003	0.06667
<i>vw</i>	0.07068	012	0.07063
<i>vw</i>	0.07268	112	0.07271
<i>w</i>	0.07471	210	0.07466
<i>w</i>	0.07570	211	0.07574
<i>vw</i>	0.08139	203	0.08134
<i>vw</i>	0.08464	103	0.08459
<i>vw</i>	0.08541	112	0.08538
<i>w</i>	0.08639	302	0.08637
<i>vw</i>	0.08833	211	0.08840
<i>vw</i>	0.09170	212	0.09163
<i>vvw</i>	0.09268	301	0.09264
<i>vvw</i>	0.10654	113	0.10659
<i>vvw</i>	0.10751	013	0.10767
<i>m</i>	0.13897	402	0.13894
<i>m</i>	0.13971	104	0.13961
<i>st</i>	0.16399	020	0.16399

The  $h0l$  and  $h1l$  reflexions were recorded with copper radiation on an integrating Weissenberg goniometer using the multiple-film technique, and estimations of intensity were made visually by means of a standard scale. The scattering curves for  $\text{Ti}^{3+}$  (Freeman and Watson, 1959) adjusted to  $\text{Ti}^{4+}$  at low angles, for  $\text{Na}^+$  (Freeman, 1959) and for  $\text{O}^{2-}$  (Suzuki, 1960) were used for the structure-factor calculations.

## Structure determination

A simple orthogonal sub-cell with strong similarities

Table 3. Comparison between observed and calculated structure factors

<i>hkl</i>	$F_o$	$F_c$	<i>hkl</i>	$F_o$	$F_c$	<i>hkl</i>	$F_o$	$F_c$	<i>hkl</i>	$F_o$	$F_c$
001	< 32	15	305	105	$\overline{101}$	703	115	77	113	54	54
002	61	$\overline{60}$	306	203	$\overline{245}$	702	128	123	114	< 39	$\overline{14}$
003	149	151	307	< 46	38	701	47	62	115	52	55
004	66	50	308	< 49	$\overline{31}$	700	47	48	116	116	141
005	< 37	22	309	94	90	701	98	92	117	< 56	18
006	92	93	3,0, $\overline{10}$	< 43	23	702	47	$\overline{33}$	118	< 59	$\overline{1}$
007	79	89	3,0, $\overline{11}$	< 32	$\overline{13}$	703	< 47	31	119	74	96
008	< 49	5	409	< 34	$\overline{14}$	704	115	136	1,1, $\overline{10}$	59	47
009	< 47	6	408	104	$\overline{98}$	705	< 47	34	219	< 52	16
0,0,10	< 41	21	407	< 47	10	706	< 47	$\overline{31}$	218	74	$\overline{71}$
0,0,11	< 31	$\overline{3}$	406	< 46	14	707	< 46	46	217	83	$\overline{75}$
1,0,11	30	37	405	104	$\overline{101}$	708	101	96	216	< 56	43
1,0,10	115	115	404	104	85	709	< 29	$\overline{16}$	215	60	$\overline{21}$
109	< 44	12	403	< 40	18	7,0, $\overline{10}$	< 26	$\overline{19}$	214	136	$\overline{136}$
108	< 49	3	402	106	$\overline{111}$	805	< 34	19	213	< 40	38
107	129	136	401	117	$\overline{139}$	804	< 40	7	212	< 34	$\overline{26}$
106	< 43	$\overline{15}$	400	89	90	803	44	73	211	74	$\overline{93}$
105	65	79	401	< 32	4	802	< 45	13	210	63	$\overline{80}$
104	288	328	402	292	$\overline{315}$	801	< 41	$\overline{24}$	211	93	$\overline{96}$
103	106	111	403	< 34	7	800	69	71	212	66	78
102	< 40	$\overline{22}$	404	< 37	$\overline{11}$	801	69	75	213	< 36	$\overline{3}$
101	89	101	405	112	$\overline{101}$	802	69	$\overline{43}$	214	< 40	4
100	93	116	406	< 44	2	803	< 47	$\overline{3}$	215	76	80
101	43	$\overline{33}$	407	< 47	11	804	83	89	216	73	80
102	< 21	9	408	< 49	0	805	< 47	$\overline{13}$	217	< 56	21
103	107	83	409	< 44	$\overline{26}$	806	< 44	0	218	< 59	$\overline{42}$
104	< 31	23	4,0, $\overline{10}$	< 41	$\overline{26}$	807	< 41	17	219	< 58	$\overline{5}$
105	< 35	18	4,0, $\overline{11}$	< 31	9	808	< 37	4	2,1, $\overline{10}$	< 52	11
106	< 44	$\overline{15}$	509	26	$\overline{34}$	809	< 27	13	319	< 45	$\overline{24}$
107	< 46	$\overline{33}$	508	96	$\overline{98}$	904	< 35	2	318	84	78
108	< 49	$\overline{31}$	507	< 44	13	903	40	61	317	59	$\overline{64}$
109	50	$\overline{50}$	506	< 47	$\overline{23}$	902	< 42	$\overline{29}$	316	< 58	27
1,0, $\overline{10}$	43	64	505	119	$\overline{130}$	901	< 43	$\overline{26}$	315	63	$\overline{62}$
1,0, $\overline{11}$	< 32	40	504	66	41	900	< 44	$\overline{36}$	314	108	$\overline{155}$
2,0,10	< 35	28	503	88	71	901	< 44	$\overline{19}$	313	52	43
209	75	$\overline{75}$	502	167	$\overline{176}$	902	< 44	$\overline{6}$	312	< 40	$\overline{1}$
208	114	107	501	< 40	$\overline{28}$	903	< 44	$\overline{16}$	311	52	48
207	83	87	500	< 38	7	904	< 43	7	310	< 34	2
206	< 44	13	501	75	$\overline{67}$	905	< 41	38	311	< 34	17
205	< 38	19	502	< 38	24	906	65	74	312	42	56
204	88	89	503	< 40	3	10,0,1	< 25	$\overline{29}$	313	64	$\overline{65}$
203	< 31	0	504	71	62	10,0,0	76	$\overline{38}$	314	50	55
202	64	$\overline{52}$	505	< 44	32	10,0, $\overline{1}$	35	44	315	< 48	$\overline{41}$
201	< 23	6	506	< 46	9	10,0,2	< 37	$\overline{29}$	316	53	55
200	21	25	507	< 49	40	10,0,3	106	99	317	< 59	12
201	87	$\overline{63}$	508	83	66	10,0,4	< 35	$\overline{44}$	318	< 59	9
202	73	45	509	< 41	19	10,0,5	< 32	34	319	< 56	66
203	93	88	5,0, $\overline{10}$	< 38	$\overline{17}$	10,0,6	83	$\overline{86}$	3,1, $\overline{10}$	< 50	14
204	32	31	5,0, $\overline{11}$	77	103	011	< 19	$\overline{1}$	419	< 37	4
205	36	58	608	< 27	0	012	75	79	418	70	$\overline{87}$
206	114	$\overline{141}$	607	64	59	013	72	94	417	< 56	18
207	< 46	23	606	44	49	014	60	56	416	< 59	15
208	< 49	7	605	< 47	$\overline{1}$	015	< 47	$\overline{35}$	415	67	55
209	113	114	604	< 47	0	016	74	82	414	< 55	13
2,0, $\overline{10}$	104	$\overline{109}$	603	< 47	$\overline{18}$	017	< 58	2	413	< 50	29
2,0, $\overline{11}$	< 34	41	602	< 45	$\overline{11}$	018	59	44	412	< 47	8
3,0,10	< 35	14	601	< 44	$\overline{16}$	019	< 56	22	411	< 44	27
309	< 40	8	600	85	51	0,1,10	88	112	410	34	31
308	< 47	37	601	92	94	1,1,10	< 44	44	411	< 40	$\overline{17}$
307	< 49	0	602	73	66	119	< 55	$\overline{26}$	412	146	$\overline{152}$
306	< 45	33	603	92	77	118	< 59	2	413	< 45	16
305	< 40	$\overline{27}$	604	89	80	117	< 58	28	414	< 48	29
304	87	$\overline{86}$	605	66	62	116	< 53	49	415	108	$\overline{133}$
303	70	56	606	48	45	115	52	55	416	< 56	27
302	< 32	$\overline{27}$	607	83	93	114	97	78	417	< 59	42
301	96	$\overline{134}$	608	114	124	113	50	33	418	83	$\overline{117}$
300	46	26	609	< 37	$\overline{23}$	112	76	92	419	< 55	34
301	< 26	$\overline{12}$	6,0, $\overline{10}$	< 34	11	111	96	$\overline{96}$	4,1, $\overline{10}$	56	31
302	197	$\overline{183}$	706	< 40	14	110	116	$\overline{142}$	518	41	28
303	74	58	705	< 42	$\overline{1}$	111	< 20	$\overline{16}$	517	< 53	32
304	76	61	704	< 46	$\overline{1}$	112	76	85	516	< 58	28

Table 3 (cont.)

<i>hkl</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	<i>hkl</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	<i>hkl</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>	<i>hkl</i>	<i>F<sub>o</sub></i>	<i>F<sub>c</sub></i>
515	59	42	613	68	57	710	< 59	16	815	< 56	3
514	< 58	29	612	113	120	711	82	80	816	< 53	26
513	< 56	37	611	< 56	19	712	< 58	28	817	99	127
512	153	161	610	< 55	4	713	< 59	8	913	60	89
511	65	64	611	82	90	714	69	60	912	< 45	9
510	56	47	612	< 55	38	715	< 59	33	911	< 48	32
511	118	133	613	< 55	21	716	< 58	4	910	115	125
512	102	101	614	< 56	50	717	64	66	911	< 53	17
513	50	57	615	< 57	55	718	64	79	912	< 53	14
514	50	55	616	< 59	17	719	< 40	10	913	91	119
515	91	92	617	< 58	27	815	< 37	16	914	51	55
516	< 58	6	618	< 55	10	814	< 45	8	915	< 48	37
517	< 59	4	619	< 48	41	813	73	81	916	< 44	30
518	64	80	6,1,10	< 37	28	812	< 55	37	10,1,0	54	73
519	< 53	34	716	81	84	811	< 58	14	10,1,1	< 40	13
5,1,10	< 44	1	715	< 50	19	810	82	89	10,1,2	< 40	11
617	49	54	714	< 54	40	811	< 59	30	10,1,3	< 40	10
616	102	95	713	< 58	32	812	< 59	14	10,1,4	< 39	15
615	81	84	712	< 59	40	813	< 59	23	10,1,5	< 34	11
614	< 59	29	711	< 59	1	814	116	130			

to a perovskite structure type could easily be recognized. The real cell is related to this by the index matrix,

$$20\bar{1}/010/\bar{1}0\bar{2}$$

and from this expression a simple trial-and-error procedure led readily to a structure for the compound in terms of an idealised octahedral model agreeing with the chemical formula, the unit cell size and with its spacegroup alternatives. The Patterson function  $P(u, w)$  was then used to derive the positions of the metal atoms more precisely since, in structures of this kind, they seldom occupy the exact centres of idealised octahedra.

The space groups  $P2_1$  and  $P2_1/m$  (Table 1) are both centro-symmetrical in projection on (010). The atomic parameters, obtained from the Patterson function, were refined by successive electron-density and difference Fourier projections on to this plane, and a final value of the reliability factor of 13.2% was reached, the non-observed terms being omitted. The parameters  $x$  and  $z$  for each atom were next combined with the constant  $y = \frac{1}{2}b$  required by the space group  $P2_1/m$  in a set of  $hkl$  structure factors, to give a reliability of 14.9% on comparison with the observations. This was considered to be adequate proof of this space

group, and no attempt was made to introduce different values for  $y$  which would be required by the possible alternative  $P2_1$ .

Table 4. Fractional atomic parameters

All atoms in general positions 2(c) for  $P2_1/m$ ,  $\pm x, \frac{1}{2}, z$

Atom	$x$	$z$	Atom	$x$	$z$
Na <sub>1</sub>	0.682	0.595	O <sub>2</sub>	0.140	0.473
Na <sub>2</sub>	0.508	0.154	O <sub>3</sub>	0.438	0.645
Ti <sub>1</sub>	0.0278	0.2806	O <sub>4</sub>	0.314	0.885
Ti <sub>2</sub>	0.2467	0.6730	O <sub>5</sub>	0.997	0.745
Ti <sub>3</sub>	0.1420	0.9811	O <sub>6</sub>	0.791	0.313
O <sub>1</sub>	0.221	0.195	O <sub>7</sub>	0.905	0.031

No isotropic temperature factor was found on comparison of the observed and calculated structure factors (Table 3), and it is possible that the effects of thermal motion are approximately cancelled by some absorption within the crystal. The atomic positions are given in Table 4 and the interatomic distances in Table 5. The final difference synthesis was used to obtain values for the accuracy of the atomic positions by methods outlined in Lipson & Cochran (1953; p. 307 et seq.); these are not included in Table 4 but are averaged for all atoms of the same kind, leading to average standard deviations for Ti-O of  $\pm 0.025$  Å,

Table 5. Interatomic distances in Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub>

No.	Length	No.	Length	No.	Length	No.	Length
Ti <sub>1</sub> -O <sub>1</sub>	1 1.97 Å	Ti <sub>2</sub> -O <sub>3</sub>	1 1.71 Å	Ti <sub>3</sub> -O <sub>4</sub>	1 1.86 Å	Na <sub>1</sub> -O <sub>2</sub>	2 2.59 Å
Ti <sub>1</sub> -O <sub>2</sub>	1 1.83	Ti <sub>2</sub> -O <sub>4</sub>	1 1.91	Ti <sub>3</sub> -O <sub>1</sub>	1 1.93	Na <sub>1</sub> -O <sub>1</sub>	2 2.71
Ti <sub>1</sub> -O <sub>6</sub>	1 2.11	Ti <sub>2</sub> -O <sub>2</sub>	1 1.87	Ti <sub>3</sub> -O <sub>7</sub> <sup>1</sup>	1 2.17	Na <sub>1</sub> -O <sub>3</sub>	2 2.93
Ti <sub>1</sub> -O <sub>7</sub>	1 2.31	Ti <sub>2</sub> -O <sub>5</sub>	1 2.34	Ti <sub>3</sub> -O <sub>5</sub>	1 2.25	Na <sub>1</sub> -O <sub>3</sub> <sup>1</sup>	1 2.23
Ti <sub>1</sub> -O <sub>5</sub>	2 1.92	Ti <sub>2</sub> -O <sub>6</sub>	2 1.94	Ti <sub>3</sub> -O <sub>7</sub>	2 1.94	Na <sub>1</sub> -O <sub>5</sub>	1 2.80
O <sub>1</sub> -O <sub>2</sub>	1 2.76	O <sub>2</sub> -O <sub>5</sub>	1 2.97	O <sub>1</sub> -O <sub>7</sub> <sup>1</sup>	1 2.82	Na <sub>1</sub> -O <sub>6</sub>	1 2.91
O <sub>1</sub> -O <sub>7</sub>	1 2.82	O <sub>2</sub> -O <sub>3</sub>	1 2.72	O <sub>1</sub> -O <sub>4</sub>	1 3.09		
O <sub>7</sub> -O <sub>6</sub>	1 2.93	O <sub>3</sub> -O <sub>4</sub>	1 2.62	O <sub>5</sub> -O <sub>7</sub> <sup>1</sup>	1 2.89	Na <sub>2</sub> -O <sub>1</sub>	1 2.56
O <sub>2</sub> -O <sub>6</sub>	1 3.11	O <sub>4</sub> -O <sub>5</sub>	1 2.74	O <sub>5</sub> -O <sub>4</sub> <sup>1</sup>	1 2.74	Na <sub>2</sub> -O <sub>4</sub> <sup>1</sup>	1 2.68
O <sub>5</sub> -O <sub>6</sub>	2 2.74	O <sub>6</sub> -O <sub>5</sub>	2 2.74	O <sub>7</sub> -O <sub>7</sub> <sup>1</sup>	2 2.64	Na <sub>2</sub> -O <sub>6</sub>	1 2.57
O <sub>5</sub> -O <sub>7</sub>	2 2.79	O <sub>6</sub> -O <sub>2</sub>	2 2.71	O <sub>7</sub> -O <sub>5</sub>	2 2.79	Na <sub>2</sub> -O <sub>4</sub>	2 2.51
O <sub>5</sub> -O <sub>1</sub>	2 2.77	O <sub>6</sub> -O <sub>3</sub>	2 2.81	O <sub>7</sub> -O <sub>4</sub>	2 2.88	Na <sub>2</sub> -O <sub>3</sub>	2 2.62
O <sub>5</sub> -O <sub>2</sub>	2 2.84	O <sub>6</sub> -O <sub>4</sub>	2 2.65	O <sub>7</sub> -O <sub>1</sub>	2 2.85		

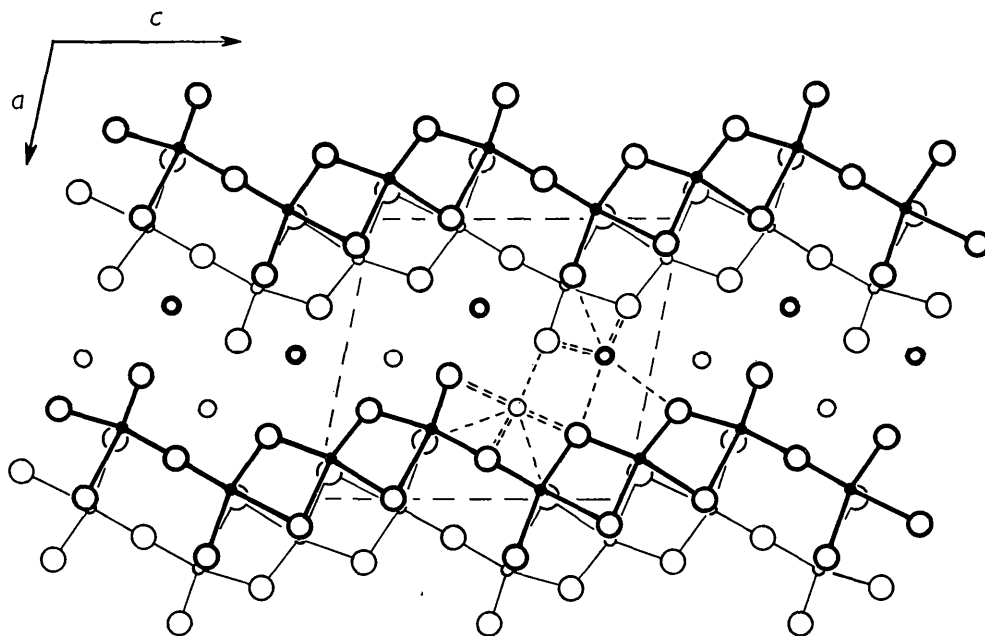


Fig. 1. The structure of  $\text{Na}_2\text{Ti}_3\text{O}_7$  seen in projection down the  $b$  axis. Bonds to oxygen (large circles) from titanium (small circles) are shown, the lighter circles representing atoms at the level  $y = \frac{1}{2}$ , the heavier at  $y = \frac{3}{2}$ . The bonds from sodium (medium circles) to oxygen are drawn as dotted lines, and the unit cell is shown in outline.

$\text{O}-\text{O} \pm 0.045 \text{ \AA}$  and  $\text{Na}-\text{O} \pm 0.030 \text{ \AA}$ . These are in good agreement with the more extensive data on  $\text{K}_2\text{Ti}_2\text{O}_5$  (Andersson & Wadsley, 1961) based on a least squares assessment.

### Description

The crystal structure of  $\text{Na}_2\text{Ti}_3\text{O}_7$  is shown diagrammatically in Fig. 1. The basic unit, seen in projection, is a block of six  $\text{TiO}_6$  octahedra, three at one level, three at a distance  $b/2 \text{ \AA}$  above (and below) which are joined by having edges in common. This extends out of the plane of the paper as a zig-zag ribbon of octahedra limited to three in width. Identical blocks are joined together by having corners in common to form a two-dimensional sheet of the composition  $(\text{Ti}_3\text{O}_7)^{2-}$  centred on the (100) plane.

There is considerable variation in the Ti-O distances for all of the metal atoms (Table 5) which may perhaps be interpreted as a tendency towards five coordination for titanium. This is the most noticeable for  $\text{Ti}_2$  where five bonds to oxygen vary between 1.71 and 1.94  $\text{\AA}$ , the sixth being 2.34  $\text{\AA}$ . The five closer oxygens form a distorted trigonal bipyramidal grouping. Although there is some ambiguity about describing a distorted geometrical figure in a closely bonded structure such as this one, the bipyramid has nevertheless been firmly established for  $\text{Ti}^{4+}$  in  $\text{K}_2\text{Ti}_2\text{O}_5$  (Andersson and Wadsley, 1960) and possibly can occur in other titanium compounds as well (Martin and Winter, 1960).

The layers are packed together in such a way as to form two different kinds of position for the sodium

atoms.  $\text{Na}_1$  has a rather unusual oxygen arrangement which, to a first approximation, can be described as a

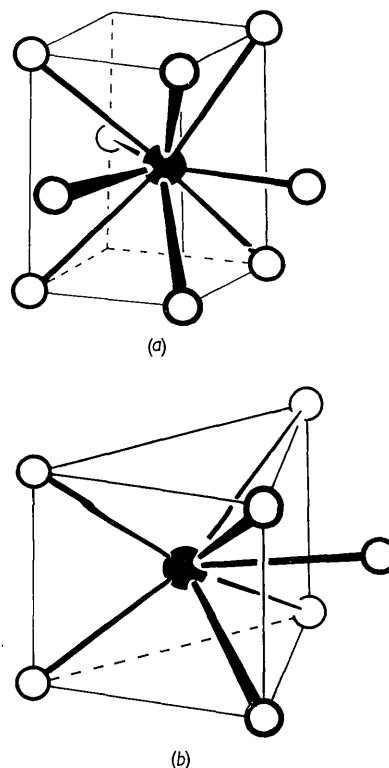


Fig. 2. Clinographic projection of the ninefold coordination of  $\text{Na}_1$  (a) and the sevenfold coordination of  $\text{Na}_2$  (b).

cube, but with two oxygens replaced by a single one at the centre of the edge from which they are missing. Outside the faces opposite this atom are two additional oxygens which complete the irregular ninefold coordination (Fig. 2(a)). The second sodium atom, Na<sub>2</sub>, is situated in a trigonal prism of oxygens, whilst a seventh oxygen is bonded through the centre of one of the rectangular prism faces (Fig. 2(b)), as in Na<sub>2-x</sub>V<sub>6</sub>O<sub>15</sub> (Wadsley, 1955).

If each alternate sheet of TiO<sub>6</sub> octahedra could be displaced upwards by a distance  $b/2$ , both of the sodium atoms could find nearly regular cubic positions for themselves. The effect of this would be to impose another space group upon the structure in which the  $a$  axis is doubled, the titanium and oxygen positions, in projection, remaining as they are. Several unsuccessful attempts were made to prepare this substance by the prolonged heat treatment of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> at a variety of temperatures as well as by quenching, but for reasons which are not at all obvious, the sodium ions do not influence the structure in favour of the proposed dimorph which would appear to have a more reasonable structure.

As a whole, Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> has certain similarities to Li<sub>1+x</sub>V<sub>3</sub>O<sub>8</sub> (Wadsley, 1957), which consists of layers made up from distorted VO<sub>6</sub> octahedra one of which can almost certainly be regarded as a trigonal bipyramid. These layers are held together by lithium atoms occupying octahedral positions, and also, perhaps, some of the tetrahedral spaces which are also present.

### Discussion

The prominent sub-cell which proved to be so useful in solving the structure, could be regarded as pseudo-cubic and related to perovskite, ABO<sub>3</sub>. In this simple structure the  $B$  atoms form oxygen octahedra which, by sharing all corners with similar octahedra, create cubic, or perhaps twelve-coordinated, sites for the  $A$  atoms.

The formation of a sub-cell by Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> is due to three structural features.

- (a) The oxygen and sodium atoms form an approximately square lattice in projection down the  $b$  axis which is similar to the projection of the perovskite lattice, except in terms of the relative positions of the atoms of different kinds.
- (b) Titanium overlies some of the positions in which oxygen alone occurs in perovskite. This is a consequence of edge sharing.

- (c) The two kinds of sodium are both surrounded by 2 Na and 2 Ti roughly in a square, but in different ways.

The net effect of these three conditions is to force a superficial statistical resemblance to a simple structure upon a complex one which, in fact, is related to it scarcely, if at all. The partial disordering of the (Ti<sub>3</sub>O<sub>7</sub>)<sup>2-</sup> layers which occurs on quenching from high temperatures, will force upon it an even greater similarity to perovskite if Debye-Scherrer photographs alone are used for identification. This point of view, and the likelihood of the change of co-ordination number of the octahedrally grouped ion (Andersson & Wadsley, 1960), have some importance in crystallographic studies of the defect solid state, and will be given a more general treatment by us elsewhere.

The layer structure of Na<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> is reflected in its chemical properties. Weiss & Weiss (1960) recently showed that the di- and trititanates can exchange Na or K for long chain alkylammonium ions as well as for other metals, and this causes an expansion perpendicular to the sheets. Their X-ray data for a dititanate, however, indicate that the compound they actually used was a trititanate instead, the loss of sodium which we found to occur in preparation evidently being overlooked by them. The structure of K<sub>2</sub>Ti<sub>2</sub>O<sub>5</sub> does suggest that this substance might also have exchange properties. This would be difficult to observe as the compound undergoes rapid hydrolysis to form completely different phases, even on exposure to moist air (Anderson & Wadsley, 1961).

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