Identification and Characterisation of Three Novel Compounds in the Sodium–Aluminium–Oxygen System [†]

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Reactions of sodium oxide with α-Al_2O_3 have produced three novel sodium-rich aluminates, $Na_7Al_3O_8$ (triclinic, space group $P\bar{1}$), $Na_{17}Al_5O_{16}$ (monoclinic, space group Cm), and Na_5AlO_4(orthorhombic, space group $Pbca$). *X*-Ray crystal structure determinations have shown $Na_7Al_3O_8$ to consist of infinite double chains composed of Al_6O_{16} rings linked by oxygen bridges, $Na_{17}Al_5O_{16}$ to consist of discrete Al_5O_{16} chains of corner-sharing AlO_4 tetrahedra with almost linear angles about the bridging oxygens, and Na_5AlO_4 to be composed of isolated AlO_4 tetrahedra.

We have been interested in the formation of aluminates in liquid sodium primarily as a consequence of our studies on the reaction of liquid sodium with concrete. Sodium aluminates are also of current interest in the development of the sodium–sulphur battery, where degradation of the β-Al_2O_3 electrolyte in oxygen-contaminated sodium may result from the formation of sodium aluminates.

The most alkali-rich sodium aluminate reported in the literature is $NaAlO_2$, but higher aluminates have been prepared for both potassium and lithium. The crystal structures of Li_5AlO_4, in two phase modifications,[1-3] and K_3AlO_3 [4] have been determined. The compound Li_3AlO_3 has also been reported,[5] but its structure was not determined. On reaction of α-Al_2O_3 with liquid sodium containing various amounts of oxygen, we found phases other than $NaAlO_2$ were being formed, but were unidentifiable from their *X*-ray powder diffraction patterns alone.

We thus embarked on a solid-state study of the Na–Al–O system using α-Al_2O_3 and Na_2O as reactants (NaOH and Na_2CO_3 are only reactive enough to form $NaAlO_2$) which led to the identification and characterisation of three new alkali-rich sodium aluminates, $Na_7Al_3O_8$,[6] $Na_{17}Al_5O_{16}$,[7] and Na_5AlO_4,[6] with no other sodium-rich aluminates being formed under our experimental conditions. The crystal-structure determinations of these aluminates all show aluminium atoms in a tetrahedral co-ordination with oxygen and that there are interesting similarities with corresponding Na–Fe–O and Na–Ga–O systems.

Experimental

(*a*) *Solid-state Reactions.*—All reactants were commercially obtained. Sodium oxide (Alfa Inorganics Ltd.) was purified prior to use by vacuum distillation at 350 °C to remove the excess of metallic sodium present as an impurity. The α-Al_2O_3 was dried thoroughly at 600 °C before use.

The reactants were ground together in the appropriate molar ratios under an argon atmosphere in an evacuable dry-box, before being compressed to pellet form to produce an intimate mixture, placed in silver crucibles, and heated at 700 °C for between 18 and 48 h under a stream of argon. Once cooled, the products were again transferred to the dry-box so that further manipulations could be accomplished without risk of atmospheric contamination. Portions of the products were ground and examined by *X*-ray powder diffraction (the diffractometer had a facility to enable the *X*-ray chamber to be flushed with nitrogen to maintain an inert atmosphere) and the remainder was examined microscopically for the presence of suitable crystals for single-crystal analysis.

(*b*) *Liquid Sodium Experiments.*—The sodium was handled in an argon-filled evacuable dry-box. Weighed quantities of α-Al_2O_3 were placed in nickel crucibles and corresponding amounts of NiO were added to give the required oxygen : aluminium ratio. Nickel oxide was used as it reacts with sodium at 282 °C to give Na_2O and Ni according to equation (1).

$$NiO + 2Na \longrightarrow Na_2O + Ni \qquad (1)$$

Hence, this provided a convenient way of introducing sodium oxide free from contamination and also of easy weighing as no protection from the atmosphere was necessary. The nickel crucibles were then filled with liquid sodium containing about 5 p.p.m. oxygen from a small glass pipette and sealed into screw-topped stainless-steel crucibles to prevent sodium loss during heating. These were sealed in a stainless-steel vessel and heated at the required temperature for 7 d in order to achieve equilibrium. The crucibles were then opened in an argon-filled evacuable dry-box. Half of the sample was removed and *X*-ray powder diffraction analysis performed on the product whilst it was still contained in the sodium matrix. The remainder was heated at 350 °C under vacuum to distil off the excess of sodium and the residues were again examined by *X*-ray powder diffraction.

(*c*) *Structure Determinations.*—In all cases data were collected on a Hilger and Watts four-circle diffractometer [λ(Mo-K_{α_1}) = 0.709 26 Å], the crystals having been sealed inside 0.2-mm Lindemann glass capillaries to protect them from the atmosphere.

Crystal data.[‡] $Na_7Al_3O_8$, M = 369.9, triclinic, a = 7.972(1), b = 5.851(1), c = 11.272(3) Å, α = 89.71(4), β = 110.57(2), γ = 108.99(2)°, U = 461.79 Å^3, Z = 2, D_c = 2.66 g cm^{-3}, $F(000)$ = 360, μ(Mo-K_{α_1}) = 7.91 cm^{-1}, space group $P\bar{1}$; R = 0.0327, and R' = 0.0361 for 1 569 independent reflections with intensities $I > 3\sigma(I)$ in the range $1 < \theta < 27°$.

$Na_{17}Al_5O_{16}$, M = 781.7, monoclinic, a = 5.961(1), b = 32.769(5), c = 5.989(1) Å, β = 120.07(2)°, U = 1 012.42 Å^3, Z = 2, D_c = 2.56 g cm^{-3}, $F(000)$ = 760, μ(Mo-K_{α_1}) = 7.48 cm^{-1}, space group Cm; R = 0.0538 and R' = 0.0630 for 676 independent reflections with $I > 3\sigma(I)$ in the range $1 < \theta < 30°$.

Na_5AlO_4, M = 205.9, orthorhombic, a = 5.894(1), b =

[†] *Supplementary data available* (No. SUP 23818, 39 pp.): thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

[‡] $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o|$, R' = Hamilton weighted R value.

Table 1. Atomic co-ordinates for $Na_7Al_3O_8$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Na(1)	0.692 6(2)	0.446 6(3)	0.762 3(1)	Al(3)	0.299 6(1)	0.069 2(2)	0.135 7(1)
Na(2)	−0.087 5(2)	−1.371 9(3)	0.555 9(1)	O(1)	0.010 2(3)	−1.463 4(4)	0.769 8(2)
Na(3)	0.483 0(2)	−0.277 2(3)	0.552 4(1)	O(2)	0.366 8(4)	−0.681 2(4)	0.582 5(2)
Na(4)	0.900 1(2)	0.151 7(3)	0.056 5(1)	O(3)	0.556 7(4)	0.020 8(5)	0.728 5(2)
Na(5)	0.509 3(2)	0.744 6(3)	0.056 5(1)	O(4)	0.200 4(3)	−1.219 9(4)	0.535 7(2)
Na(6)	0.707 8(2)	0.471 4(3)	0.270 8(1)	O(5)	0.215 7(4)	−0.911 5(5)	0.760 1(2)
Na(7)	0.901 9(2)	0.659 2(3)	0.051 6(1)	O(6)	0.404 7(4)	0.359 8(4)	0.104 2(2)
Al(1)	0.093 9(1)	−1.165 3(2)	0.840 6(1)	O(7)	0.097 4(4)	0.068 9(5)	0.165 9(2)
Al(2)	0.324 9(1)	−0.958 5(2)	0.645 7(1)	O(8)	0.767 8(4)	0.152 6(5)	−0.004 6(2)

Table 2. Bond lengths (Å) and selected angles (°) for $Na_7Al_3O_8$ with standard deviations in parentheses

Al(1)–O(1)	1.734(3)	Al(3)–O(8)	1.779(3)	Na(3)–O(2)	2.298(3)	Na(6)–O(1)	2.461(3)
Al(1)–O(5)	1.775(3)	Na(1)–O(1)	2.383(3)	Na(3)–O(3)	2.424(3)	Na(6)–O(2)	2.404(3)
Al(1)–O(7)	1.769(3)	Na(1)–O(2)	2.543(3)	Na(3)–O(4)	2.327(3)	Na(6)–O(4)	2.646(3)
Al(1)–O(8)	1.776(3)	Na(1)–O(3)	2.343(3)	Na(4)–O(1)	2.281(3)	Na(6)–O(5)	2.722(3)
Al(2)–O(2)	1.747(3)	Na(1)–O(6)	2.357(3)	Na(4)–O(4)	2.226(3)	Na(6)–O(6)	2.364(3)
Al(2)–O(3)	1.798(3)	Na(1)–O(7)	2.734(3)	Na(4)–O(5)	2.631(3)	Na(7)–O(1)	2.316(3)
Al(2)–O(4)	1.740(3)	Na(2)–O(1)	2.376(3)	Na(4)–O(7)	2.272(3)	Na(7)–O(6)	2.425(3)
Al(5)–O(5)	1.798(3)	Na(2)–O(2)	2.344(3)	Na(5)–O(5)	2.379(3)	Na(7)–O(7)	2.454(3)
Al(3)–O(3)	1.756(3)	Na(2)–O(4)	2.269(3)	Na(5)–O(6)	2.266(3)	Na(7)–O(8)	2.795(3)
Al(3)–O(6)	1.730(3)	Na(2)–O(4)	2.357(3)	Na(5)–O(6)	2.298(3)	Na(7)–O(8)	2.741(3)
Al(3)–O(7)	1.761(3)	Na(3)–O(2)	2.313(3)	Na(6)–O(1)	2.353(3)		

O(1)–Al(1)–O(5)	113.4(1)	O(2)–Al(2)–O(3)	105.6(1)	O(3)–Al(3)–O(6)	114.5(1)	Al(2)–O(3)–Al(3)	145.4(2)
O(1)–Al(1)–O(7)	110.9(1)	O(2)–Al(2)–O(4)	116.3(1)	O(3)–Al(3)–O(7)	106.3(1)	Al(1)–O(5)–Al(2)	136.9(2)
O(1)–Al(1)–O(8)	108.4(1)	O(2)–Al(2)–O(5)	109.4(1)	O(3)–Al(3)–O(8)	107.2(1)	Al(1)–O(7)–Al(3)	157.1(2)
O(5)–Al(1)–O(7)	103.4(1)	O(3)–Al(2)–O(4)	104.8(1)	O(6)–Al(3)–O(7)	106.7(1)	Al(1)–O(8)–Al(3)	130.1(1)
O(5)–Al(1)–O(8)	113.4(1)	O(3)–Al(2)–O(5)	108.4(1)	O(6)–Al(3)–O(8)	111.4(1)		
O(7)–Al(1)–O(8)	106.9(1)	O(4)–Al(2)–O(5)	111.7(1)	O(7)–Al(3)–O(8)	110.3(1)		

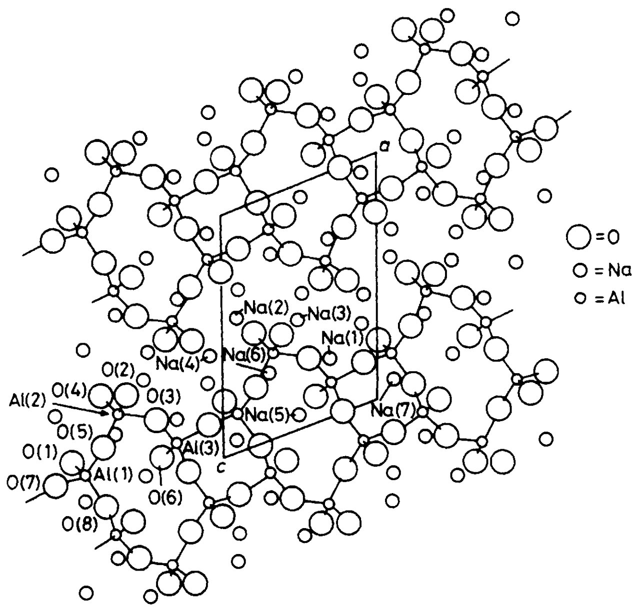

Figure 1. The crystal structure of $Na_7Al_3O_8$ viewed along the *b* axis

17.870(4), c = 10.095(3) Å, U = 1 063.3 Å^3, Z = 8, D_c = 2.57 g cm^{-3}, $F(000)$ = 800, μ(Mo-K_{α_1}) = 7.38 cm^{-1}, space group *Pbca*; R = 0.034 and R' = 0.037 for 598 independent reflections with $I > 3\sigma(I)$ in the range $1 < \theta < 25°$.

Refinement. The initial atomic co-ordinates of $Na_7Al_3O_8$ had to be found using direct methods by means of the MULTAN 78 program.[8] This correctly located the positions of four Na, two Al, and five oxygen atoms. Fourier syntheses phased on these co-ordinates using the CRYSTALS program [9] revealed the position of all the remaining atoms. After complete refinement, a Fourier difference electron-density synthesis showed no significant peaks. The structure is shown in Figure 1 projected along the *b* axis. The atomic co-ordinates are listed in Table 1 and the bond distances and angles in Table 2.

The solution of the structure of $Na_{17}Al_5O_{16}$ was not as straightforward in that the use of direct methods was unsuccessful. We, therefore, had to resort to interpretation of a sharpened Patterson map taken in X, Z sections, in spite of there being no heavy atoms involved. Identification of two vectors at the right distance and angle for Al–O vectors at Y = 0.0, together with packing considerations, enabled us to find the approximate positions of all the atoms in the Al–O framework, placing Al(1) on the mirror plane at 0,0,0 since the position of the origin is arbitrary in space group *Cm*. Fourier syntheses phased on these positions yielded all the sodium atoms and a difference Fourier showed no significant peaks after completion of the refinement. The structure, viewed along the *c* axis, is shown in Figure 2, and atomic co-ordinates, bond lengths and angles are listed in Tables 3 and 4 respectively.

The structure of Na_5AlO_4 was solved initially using the MULTAN program which located the positions of four Na, one Al, and three O atoms. The remaining positions were found as before using CRYSTALS. Again there were no significant peaks on the difference Fourier after refinement. Figure 3 shows the structure viewed down the *a* axis, and the atomic co-ordinates, bond lengths and angles are listed in Tables 5 and 6 respectively.

Table 3. Atomic co-ordinates for $Na_{17}Al_5O_{16}$

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Na(1)	−0.031(3)	0.323 8(3)	0.466(3)	Al(3)	−0.010(3)	0.180 4(2)	−0.005(3)
Na(2)	0.488(4)	0.0000	0.489(4)	O(1)	0.308(4)	0.0000	0.031(5)
Na(3)	0.107(3)	0.453 9(3)	0.078(3)	O(2)	0.001(5)	0.0000	0.286(6)
Na(4)	0.050(3)	0.137 5(4)	0.584(3)	O(3)	−0.179(5)	0.043 1(6)	−0.171(4)
Na(5)	0.090(3)	0.361 9(4)	0.062(3)	O(4)	−0.619(4)	0.093 9(5)	−0.342(4)
Na(6)	0.076(3)	0.046 2(3)	0.614(3)	O(5)	−0.354(3)	0.093 1(4)	10.632(3)
Na(7)	0.193(3)	0.008 1(3)	0.195(3)	O(6)	−0.124(4)	0.130 2(5)	−0.116(3)
Na(8)	0.111(3)	0.270 6(3)	0.052(3)	O(7)	0.295(4)	0.184 7(4)	0.011(4)
Na(9)	0.072(3)	0.225 1(3)	0.625(3)	O(8)	−0.010(4)	0.186 3(5)	0.278(3)
Al(1)	0.0000	0.0000	0.0000	O(9)	0.277(4)	0.284 2(4)	0.772(3)
Al(2)	−0.326(2)	0.089 7(2)	−0.323(2)				

Table 4. Bond lengths (Å) and angles (°) for $Na_{17}Al_5O_{16}$ with standard deviations in parentheses

Al(1)–O(1)	1.75(2)	Na(1)–O(6)	2.89(2)	Na(5)–O(4)	2.55(2)	Na(8)–O(7)	2.30(2)
Al(1)–O(2)	1.71(3)	Na(1)–O(7)	2.40(2)	Na(5)–O(5)	2.24(2)	Na(8)–O(8)	2.42(2)
Al(1)–O(3)	1.75(2)	Na(1)–O(8)	2.51(2)	Na(5)–O(6)	2.43(2)	Na(8)–O(9)	2.38(2)
Al(1)–O(3)	1.76(2)	Na(1)–O(9)	2.25(2)	Na(5)–O(7)	2.23(2)	Na(8)–O(9)	2.58(2)
				Na(5)–O(8)	2.60(2)		
Al(2)–O(3)	1.77(2)	Na(2)–O(1)	2.39(3)			Na(3)–O(1)	2.24(2)
Al(2)–O(4)	1.70(2)	Na(2)–O(2)	2.53(3)	Na(6)–O(1)	2.64(2)	Na(3)–O(2)	2.53(2)
Al(2)–O(5)	1.78(1)	Na(2)–O(3)	2.45(3)	Na(6)–O(2)	2.34(2)	Na(3)–O(3′)	2.39(3)
Al(2)–O(6)	1.80(2)	Na(2)–O(3)	2.45(3)	Na(6)–O(3)	2.45(2)	Na(3)–O(4)	2.68(2)
				Na(6)–O(4)	2.31(2)	Na(3)–O(5)	2.25(2)
Al(3)–O(6)	1.78(2)	Na(4)–O(4)	2.29(2)	Na(6)–O(5)	2.70(2)		
Al(3)–O(7)	1.78(1)	Na(4)–O(5)	2.54(2)			Na(9)–O(7)	2.40(2)
Al(3)–O(8)	1.71(2)	Na(4)–O(6)	2.49(2)	Na(7)–O(3)	2.65(2)	Na(9)–O(8)	2.27(2)
Al(3)–O(9)	1.74(1)	Na(4)–O(7)	2.70(2)	Na(7)–O(4)	2.42(2)	Na(9)–O(9)	2.22(2)
		Na(4)–O(8)	2.32(2)	Na(7)–O(5)	2.37(2)	Na(9′)–O(9′)	2.25(2)
				Na(7)–O(6)	2.32(2)		

O(1)–Al(1)–O(2)	114(1)	O(3)–Al(2)–O(4)	109(1)	O(6)–Al(3)–O(7)	106.4(8)
O(1)–Al(1)–O(3)	111(1)	O(3)–Al(2)–O(5)	110.9(9)	O(6)–Al(3)–O(8)	106.6(8)
O(1)–Al(1)–O(3′)	111(1)	O(3)–Al(2)–O(6)	107.1(9)	O(6)–Al(3)–O(9)	109.7(8)
O(2)–Al(1)–O(3)	106(1)	O(4)–Al(2)–O(5)	111.6(7)	O(7)–Al(3)–O(8)	116.5(7)
O(2)–Al(1)–O(3′)	106(1)	O(4)–Al(2)–O(6)	107.2(9)	O(7)–Al(3)–O(9)	108.8(7)
O(3)–Al(1)–O(3′)	106(1)	O(5)–Al(2)–O(6)	110.6(7)	O(8)–Al(3)–O(9)	108.8(8)
		Al(1)–O(3)–Al(2)	173(1)		
		Al(2)–O(6)–Al(3)	159.5(9)		
		Al(1)–O(3)–Al(2)	173(1)		
		Al(2)–O(6)–Al(3)	159.5(9)		

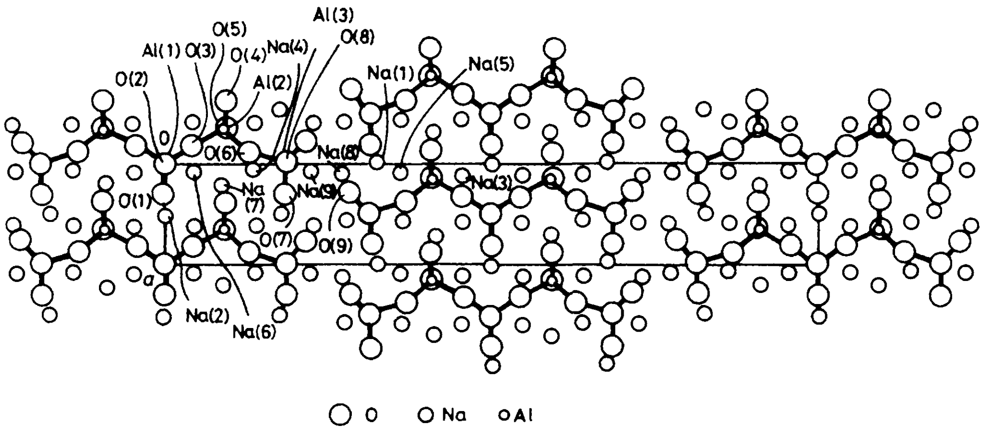

Figure 2. The crystal structure of $Na_{17}Al_5O_{16}$ viewed along the *c* axis

Results

(*a*) *Solid-state Reactions.*—The *X*-ray powder diffraction patterns obtained from these reactions were complex, and were not to be found in the J.C.P.D.S. files. However, from the single-crystal data obtained from the three crystal structure determinations it was possible to produce simulated powder patterns for the three compounds using the POWD program.[10] These were in excellent agreement with the experimental

Table 5. Atomic co-ordinates for Na_5AlO_4

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
Na(1)	0.894 0(4)	0.173 4(1)	0.673 2(2)	Al(1)	0.765 2(6)	0 126 6(2)	0.869 7(3)
Na(2)	1.089 7(4)	0.064 3(1)	0.938 3(2)	O(1)	0.803 7(6)	0.048 7(2)	1.125 8(4)
Na(3)	0.912 1(4)	0.001 1(1)	1.339 7(2)	O(2)	0.764 2(6)	0.207 9(2)	1.122 3(4)
Na(4)	0.895 0(4)	0.250 3(1)	0.916 6(3)	O(3)	0.083 6(4)	0.137 2(1)	0.198 6(2)
Na(5)	0.678 7(3)	0.124 17(9)	1.039 1(2)	O(4)	0.380 5(6)	0.119 2(2)	0.045 8(4)

Table 6. Bond lengths (Å) and angles (°) for Na_5AlO_4 with standard deviations in parentheses

Al–O(1)	1.784(4)	Na(2)–O(1)	2.319(4)	Na(4)–O(1)	2.387(5)	O(1)–O(2)	2.945(5)
Al–O(2)	1.768(4)	Na(2)–O(2)	2.550(4)	Na(4)–O(3)	2.341(5)	O(1)–O(3)	2.934(5)
Al–O(3)	1.789(4)	Na(2)–O(2)	2.213(4)	Na(4)–O(3)	2.334(4)	O(1)–O(4)	2.884(5)
Al–O(4)	1.761(4)	Na(2)–O(4)	2.253(4)	Na(4)–O(4)	2.364(4)		
						O(2)–O(3)	2.854(5)
Na(1)–O(1)	2.283(4)	Na(3)–O(1)	2.529(5)	Na(5)–O(2)	2.400(4)		
Na(1)–O(1)	2.382(5)	Na(3)–O(2)	2.407(4)	Na(5)–O(3)	2.395(4)	O(3)–O(4)	2.868(5)
Na(1)–O(3)	2.313(4)	Na(3)–O(2)	2.484(5)	Na(5)–O(3)	2.449(4)		
Na(1)–O(4)	2.416(4)	Na(3)–O(4)	2.413(4)	Na(5)–O(4)	2.354(4)		

O(1)–Al–O(2)	111.9(2)	O(2)–Al–O(3)	106.7(2)	O(3)–Al–O(4)	107.8(2)
O(1)–Al–O(3)	110.4(2)	O(2)–Al–O(4)	110.9(2)		
O(1)–Al–O(4)	108.8(2)				

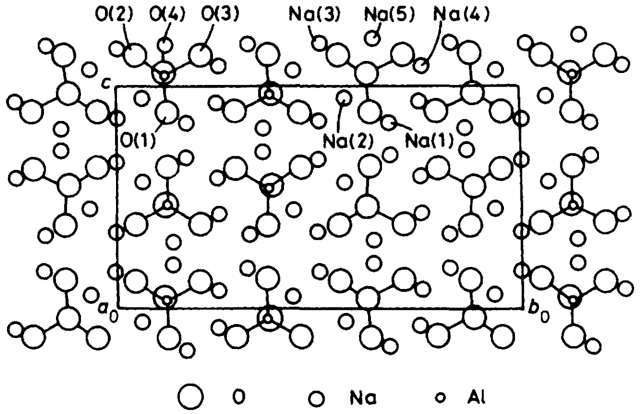

Figure 3. The crystal structure of Na_5AlO_4 viewed along the a axis

Table 7. Solid-state reactions

Ratio Na_2O : Al_2O_3	θ_c/°C	t/h	Products identified
1 : 1	700	18	$NaAlO_2$
3 : 2	700	18	$NaAlO_2$
2 : 1	700	18	$NaAlO_2$, $Na_7Al_3O_8$
7 : 3	700	18	$Na_7Al_3O_8$
5 : 2	700	18	$Na_7Al_3O_8$
3 : 1	800	48	$Na_{17}Al_5O_{16}$, X
7 : 2	800	48	$Na_{17}Al_5O_{16}$
4 : 1	700	12	$Na_{17}Al_5O_{16}$
5 : 1	700	18	$Na_{17}Al_5O_{16}$, Na_5AlO_4, X

X = Unidentified phase.

patterns and enabled the assignment of all peaks belonging to these three compounds. This showed that the major phases present were β-$NaAlO_2$, $Na_7Al_3O_8$, $Na_{17}Al_5O_{16}$, and Na_5AlO_4. The phases identified in each reaction are given in Table 7 and the observed and calculated X-ray powder patterns for $Na_7Al_3O_8$, $Na_{17}Al_5O_{16}$, and Na_5AlO_4 are given in Tables 8, 9, and 10 respectively.

For $Na_2O : Al_2O_3$ ratios between 1 : 1 and 5 : 2 the only aluminates observed were β-$NaAlO_2$ and $Na_7Al_3O_8$, no evidence for the $5Al_2O_3{\cdot}2Na_2O$ compound $Na_4Al_2O_5$ being observed. It was therefore concluded that this compound does not exist under the experimental conditions used. At higher Na : Al ratios certain complications arose. The X-ray trace for the 3 : 1 product showed the presence of $Na_{17}Al_5O_{16}$, but a second, unknown compound was evident and this is denoted by X. The diffraction lines on this trace were slightly broadened so that resolution of some lines of $Na_{17}Al_5O_{16}$ was not possible although the peak intensities were in agreement with the computer simulation.

Both the 4 : 1 and 7 : 2 ratios gave pure $Na_{17}Al_5O_{16}$ and the 4 : 1 trace showed some resolution of the multiplet centred at $d = 2.58$ Å. The trace from the 7 : 2 reaction was the 'cleanest' trace obtained for $Na_{17}Al_5O_{16}$, although resolution of some of the peaks was not seen. No phase X was observed in these products.

(*b*) *Liquid Sodium Reactions*.—Inspection of Table 11(*a*) shows that Al_2O_3, β-$NaAlO_2$, $Na_7Al_3O_8$, $Na_{17}Al_5O_{16}$, and Na_5AlO_4 are stable to liquid sodium and the aluminates may be formed by the reaction of Al_2O_3 with Na_2O dissolved in the sodium. The X-ray powder diffraction patterns of the products in a matrix of sodium and after the sodium had been removed by vacuum distillation were found to be identical. This comparison was necessary to eliminate the possibility that reaction had taken place between Al_2O_3 and solid Na_2O under vacuum after the excess of sodium had been removed by distillation. It is clear that, for the lower $Na_2O : Al_2O_3$ ratios, equilibrium has not been reached even after heating at 600 °C for 1 week.

It can be seen from Table 11(*a*) that, at the 2 : 1 and 3 : 1 ratios, there was not enough oxygen added to account for a full conversion of the alumina into $Na_{17}Al_5O_{16}$. It was not possible for extra oxygen to come from a vessel leak since the reactions at lower ratios, *i.e.* 1 : 2, 1 : 1, and 3 : 2, would also have been affected. In addition, the unknown phase X was observed at the 4 : 1 ratio. To help clarify these anomalies, a series of reactions, using NiO and $NaAlO_2$ as starting materials in liquid sodium [see Table 11(*b*)], were performed as it was thought that a more rapid equilibration would be possible.

Table 8. The *X*-ray powder diffraction pattern of $Na_7Al_3O_8$

hkl	$d_{calc.}$/Å	Calc. I/I_0	$d_{obs.}$/Å	Obs. I/I_0
001	10.479	10	—	—
010	5.491	12	5.47	5
002	5.239	6	5.22	10
$\bar{1}02$	5.218	12		
$0\bar{1}1$	5.129	9	5.12	8
101	5.032	6	5.03	6
$1\bar{1}1$	4.452	14	4.45	9
$\bar{1}03$	3.721	6	3.72	6
102	3.607	28	3.58	43 (unresolved multiplet)
$\bar{2}02$	3.587	36		
012	3.577	13		
$\bar{2}10$	3.564	29		
$\bar{1}\bar{1}2$	3.552	6	3.47	7
112	2.707	11	2.69	10
$\bar{2}\bar{1}2$	2.689	18	2.67	20
$\bar{2}20$	2.650	66	2.63	45
$2\bar{1}2$	2.610	6	2.60	12
$\bar{2}04$, $\bar{3}12$	2.607	9	2.59	24
$\bar{1}22$	2.577	5	2.56	12
$0\bar{2}2$	2.565	9	2.55	14
202	2.516	58	2.50	52
$\bar{3}02$	2.504	50		
$\bar{2}14$	2.490	80	2.48	100
$0\bar{1}4$	2.486	81		
022	2.318	100	2.31	70
$\bar{1}\bar{2}2$	2.305	81	2.30	55
$1\bar{1}4$, $\bar{3}14$	2.210	38	2.25	25
$3\bar{1}2$	1.997	43	1.986	25
$\bar{4}12$	1.992	59	1.975	33
$\bar{3}24$	1.933	6	1.924	7
$1\bar{2}4$	1.928	5		
310	1.924	4		
$\bar{1}32$	1.805	14	1.804	8
$0\bar{3}2$	1.798	17	1.796	13
$\bar{3}32$	1.762	5	1.754	5
$\bar{1}16$	1.744	4	1.735	3
$\bar{3}06$	1.739	3		
$\bar{2}\bar{1}6$	1.735	4		
130	1.638	6	1.635	3
016	1.608	30	1.604	17
316	1.597	24	1.595	13
106	1.565	5	1.559	5
$\bar{4}06$, $4\bar{2}2$, $\bar{5}22$	1.553	33	1.547	10
320	1.537	23	1.531	8

Table 9. The *X*-ray powder diffraction pattern of $Na_{17}Al_5O_{16}$

hkl	$d_{calc.}$/Å	Calc. I/I_0	$d_{obs.}$/Å	Obs. I/I_0
020	16.384	5	—	—
001	5.183	17	5.18	12
$\bar{1}11$	5.113	14	5.08	10
110	5.096	9	—	—
041	4.380	6		
150	4.054	24	4.047	10
061	3.759	20	3.74	10
0100	3.277	5	—	—
111	2.972	7	2.97	5
$\bar{1}52$	2.724	10	2.72	6
002	2.591	19	2.57	100
$\bar{2}02$	2.588	62		
$\bar{1}111$	2.582	100		
1110	2.579	15		
200	2.579	18		
0121	2.416	10	2.41	4
062	2.341	31	2.33	24
260	2.332	34		
1111	2.108	92	2.1	43
$\bar{2}102$ 0102	2.031	10	2.02	5
$\bar{2}03$	1.959	9	1.954	9
$\bar{1}13$	1.957	11		
$\bar{3}12$	1.949	6	1.946	9
$\bar{3}11$	1.947	10		
0161	1.905	5	—	—
$\bar{1}53$	1.878	19	1.872	11
$\bar{3}51$	1.869	19		
$\bar{1}73$	1.808	5	—	—
$\bar{3}71$	1.800	5	—	—
$\bar{3}13$	1.723	4	1.717	3
$\bar{1}113$	1.638	12	1.635	6
$\bar{3}112$	1.633	6	1.630	8
$\bar{3}111$	1.631	13		
1171	1.619	4	1.614	3
0162	1.607	8	1.601	4
2160	1.604	8		

As can be seen, however, the formation of $Na_{17}Al_5O_{16}$ was observed again even though insufficient oxygen was added initially and no satisfactory explanation can be offered as yet. The unknown phase X was again apparent, represented by the following *d* values (Å) (intensities in parentheses): 2.61(100), 2.31(40), 2.11(40), 1.94(25), 1.87(25), and 1.63(25).

(*c*) *Crystal Structures*.—The compound $Na_7Al_3O_8$ consists of AlO_4 tetrahedra sharing corners to form infinite double chains running parallel to the *a* axis. The tetrahedral angles are somewhat distorted varying between 103.4(1) and 116.3(1) and the bridging oxygens have rather larger Al–O–Al angles ranging from 130.1(1) to 157.1(2)°. The double chains consist of a series of non-planar six-membered rings which are joined on each side by two oxygen bridges. Bond lengths vary from 1.730(3) to 1.798(3) Å between aluminium and oxygen and from 2.226(3) to 2.795(3) Å between sodium and oxygen. The co-ordination of the sodium atoms is rather complex, being either four- or five-co-ordinate with non-regular angles varying from 66.31(9) to 170.1(1)°.

The compound $Na_{17}Al_5O_{16}$ is composed of isolated Al_5O_{16} chains running parallel to the *b* axis surrounded by sodium atoms. The aluminium atoms, as found in $Na_7Al_3O_8$, are tetrahedrally bound to oxygen with rather distorted angles varying from 106(1) to 116.5(7)°. Five AlO_4 tetrahedra share corners with very large angles about the bridging oxygens [173(1) and 159.5(9)°] to form the Al_5O_{16} chain. The co-ordination of the sodium atoms is again complex with Na(1), Na(2), Na(7), Na(8), and Na(9) being four-co-ordinate and the remainder five-co-ordinate, the O–Na–O angles varying from 66.2(6) to 138.0(6)°. Bond distances lie between 1.70(2) and 1.80(2) Å for Al–O and 2.22(2) and 2.89(2) Å for Na–O.

The most alkali-rich compound in the series, Na_5AlO_4, contains the smallest aluminate ion AlO_4^{5-} which is tetra-

Table 10. The *X*-ray powder diffraction pattern of Na_5AlO_4

hkl	$d_{calc.}$/Å	Calc. I/I_0	$d_{obs.}$/Å	Obs. I/I_0
021	6.691	18	6.53	15
002	5.047	22	4.95	30
111	4.895	4	4.82	3
040	4.467	28	4.38	35
121	4.422	40		
041	4.085	2	4.04	5
131	3.869	18	3.82	14
102	3.834	5	3.78	5
141, 042	3.347	6	3.30	7
200	2.947	3	2.92	5
151	2.925	3	2.88	10
210	2.908	11		
220, 211	2.796	5	2.67	5
230	2.641	35	2.62	29
133	2.623	23	2.59	46
152	2.614	39		
062	2.565	46	2.54	100
231	2.555	100		
004	2.524	19	2.51	27
240	2.459	5	2.43	10
143	2.445	11		
232	2.340	7	2.33	6
114	2.301	86	2.28	79
171	2.282	27	2.27	26
153	2.262	40	2.25	42
124	2.245	22	2.23	23
080	2.234	16		
242	2.211	7	2.20	10
213, 044	2.199	37	2.19	29
134	2.162	10	2.14	8
223	2.152	9		
172	2.125	21	2.11	15
163	2.086	10	2.08	7
144	2.059	6	2.04	20
261	2.051	20		
025	1.969	8	1.955	13
182	1.930	59	1.920	51
173, 311	1.917	5	—	—
214	1.906	12	1.897	12
271	1.895	5	—	—
321	1.885	43	1.875	34
125	1.868	8	1.861	11
191	1.849	13	1.842	10
045	1.839	7	1.826	10
331	1.834	7		
302	1.831	6		
272	1.802	8	1.796	5
262, 183	1.776	5	1.768	3
0101	1.759	10	1.751	8
342	1.694	15	1.687	15
1101	1.686	12	1.678	13
282, 273	1.675	6	1.674	8
065	1.671	20	1.661	20
323	1.667	8		

Table 11. Liquid sodium reactions

(*a*) $NiO + Al_2O_3 + Na$ [a]

Ratio $NiO : Al_2O_3$	Products identified
1 : 2	α-Al_2O_3, β-$NaAlO_2$
1 : 1	α-Al_2O_3, β-$NaAlO_2$, $Na_7Al_3O_8$
3 : 2	α-Al_2O_3, β-$NaAlO_2$, $Na_7Al_3O_8$
2 : 1	$Na_{17}Al_5O_{16}$
3 : 1	$Na_{17}Al_5O_{16}$
4 : 1	$Na_{17}Al_5O_{16}$, X
5 : 1	Na_5AlO_4

(*b*) $NiO + NaAlO_2 + Na$ [b]

Ratio $NiO : NaAlO_2$	Equiv. ratio $Na_2O : Al_2O_3$	Products identified
1 : 2	2 : 1	$Na_{17}Al_5O_{16}$
2 : 3	7 : 3	$Na_{17}Al_5O_{16}$, X (minor)
0.8 : 1	2.6 : 1	$Na_{17}Al_5O_{16}$, X
6 : 5	17 : 5	$Na_{17}Al_5O_{16}$, X

[a] 600 °C, 168 h. Products identified from samples by *X*-ray diffraction. All products showed the presence of Ni metal resulting from the reduction of the NiO which was used to add oxygen (Na_2O) to the sodium. [b] 600 °C, 336 h. Products identified as indicated in footnote *a*.

hedral [angles falling between 106.7(2) and 111.9(2)°] and completely isolated by surrounding sodium atoms. From the view in Figure 3, it can be seen that the tetrahedra occur in double rows with the same vertical orientation running parallel to the *c* axis. Adjacent tetrahedra within each row are reflected in the 001 plane with respect to each other and those in the *b*-axis direction are related by a half-rotation about the vertical axis with or without a reflection in the 100 plane. All the sodium atoms are four-co-ordinate with Na–O bond distances between 2.213(4) and 2.550(4) Å and O–Na–O angles between 73.9(1) and 159.0(2)°.

Discussion

The three new compounds described, which are the only known sodium-rich aluminates, show interesting similarities to the iron and gallium systems. The ionic radii of Al^{3+}, Ga^{3+}, and Fe^{3+} are similar (0.51, 0.62, and 0.64 Å respectively). As can be seen from Table 12, which shows the compounds that have been reported for the three sodium ternary oxide systems, the iron system has been extensively studied with single-crystal structure determinations for all except 'Na_3FeO_3.' Cell dimensions of $a = 13.37$, $b = 10.70$, $c = 6.13$ Å, and $\beta = 117.8°$ have been reported for this compound [11] but no space group or structural details. For all three systems the 1 : 1 compounds have been studied, with two or three structural modifications designated by α, β, or γ existing for $NaFeO_2$, $NaGaO_2$, and $NaAlO_2$. Compounds of the same stoicheiometry are isostructural so that Na_5FeO_4, Na_5GaO_4, and Na_5AlO_4 all belong to the space group *Pbca* and consist of isolated MO_4 tetrahedra.

Similarly, $Na_8Fe_2O_7$ and $Na_8Ga_2O_7$ are isostructural as are $Na_7Fe_3O_8$ and $Na_7Al_3O_8$. There are several interesting gaps in this table since no analogues of $Na_4Fe_2O_5$ have been observed in the gallium system and we have no evidence for the formation of the aluminium compound under our experimental conditions. We also have no evidence to suggest the existence of $Na_8Al_2O_7$ in spite of the existence of $Na_8Fe_2O_7$ and $Na_8Ga_2O_7$, although we have found the compound $Na_7Al_3O_8$. If there is a trend across the series then we might predict that

Table 12. Comparison of the known sodium-rich ferrates, gallates, and aluminates

Na–Fe–O	Ref.	Na–Ga–O	Ref.	Na–Al–O	Ref.
$Na_4Fe_2O_5$ [a]	11, *b*	—		—	
$Na_7Fe_3O_8$ [a]	*c*	$Na_7Ga_3O_8$	12	$Na_7Al_3O_8$ [a]	6
' Na_3FeO_3 '	11	' Na_3GaO_3 '	12	$Na_{17}Al_5O_{16}$ [a]	12
$Na_8Fe_2O_7$ [a]	*d*	$Na_8Ga_2O_7$ [a]	*e*	—	
Na_5FeO_4 [a]	9	Na_5GaO_4 [a]	*f*	Na_5AlO_4 [a]	6

[a] Single-crystal structure determination reported. [b] G. Brachtel and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1978, **446**, 97. [c] G. Brachtel and R. Hoppe, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 43; *Z. Anorg. Allg. Chem.*, 1978, **446**, 87. [d] G Brachtel and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1978, **438**, 15. [e] D. Fink and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1976, **122**, 1. [f] D. Fink and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1975, **414**, 193.

$Na_7Ga_3O_8$ would be a stable compound, as the radius of Ga falls between those of Al and Fe, and indeed the existence of $Na_7Ga_3O_8$ has been postulated [12] but no crystal structure has as yet been reported. It seems reasonable, however, that the smaller M^{3+} radii may cause $Na_4Ga_2O_5$, $Na_4Al_2O_5$, and $Na_8Al_2O_7$ to be unstable. These three compounds, if they exist, could be stable at lower temperatures than we have employed in this study.

The other point of interest is that no structure determinations have been carried out on Na_3FeO_3, Na_3GaO_3, or Na_3AlO_3 and it seems questionable whether these compounds exist. The reason for this may be the size of the alkali-metal cation as the compounds $K_6Al_2O_6$,[4] $K_6Fe_2O_6$,[13] $K_6Ga_2O_6$,[12] $Rb_6Ga_2O_6$,[13] and $Cs_6Ga_2O_6$ have all been reported. The existence of ' Na_3GaO_3 ' is also claimed,[12] but no successful single-crystal structure determination has been reported, the space-group determination was uncertain, and it was reported that the system was complex about the stoicheiometry 3 : 1. We have found in the aluminium system that the compound $Na_{17}Al_5O_{16}$, which corresponds to $Na_{3.4}AlO_{3.2}$, occurs over a wide range of reactant ratios and is very close to the stoicheiometry of Na_3AlO_3. If the chains of corner-sharing AlO_4 tetrahedra were infinite then it would in fact have the same stoicheiometry as Na_3AlO_3, but restriction of the chain to five tetrahedral AlO_4 units gives rise to the rather unusual observed stoicheiometry. The fact that $Na_7Al_3O_8$ consists of six corner-sharing AlO_4 tetrahedra forming a ring may indicate that five tetrahedra is the maximum number that is stable in a linear configuration. It may be that the proposed compounds Na_3GaO_3 and Na_3FeO_3 comprise M_5O_{16} chains instead of the M_2O_6 dimers of the potassium, rubidium, and caesium compounds, or of infinite chains.

The identity of compound X, although unknown at present, seems to be associated with the compound $Na_{17}Al_5O_{16}$ and indeed the *X*-ray pattern (although only the six major lines can be identified) shows similarities with $Na_{17}Al_5O_{16}$. It seems possible that it is also composed of $Al_xO_{3x+1}{}^{(3x+2)-}$ chains. A chain of three corner-linked tetrahedra would give rise to the stoicheiometry $Na_{11}Al_3O_{10}$ and four tetrahedra would give $Na_{14}Al_4O_{13}$ both of which lie within the observed Na : Al range for the occurrence of X. Indeed, the latter compound has recently been reported [14] although no structural information was given.

The other feature of these compounds worthy of mention is the Al–O–Al angles which are increased significantly from the expected tetrahedral angle. Increases of this type have been observed in several main-group and transition-metal ternary oxides and a compilation of these is given in Table 13. A convenient explanation for the angle widening is that the vacant 3*d* orbitals of aluminium are participating in π bonding leading to a strengthening of the bond and a shortening of the bond length.

The energy difference between the 3*d* and 3*p* orbitals is thought to be reduced by the presence of the highly electronegative field produced by the O atoms.[15] Also, if the *d*-orbital radial maximum is large compared to the bond lengths then the *d*-orbital contribution will be small, but again the presence of a polarising field can contract the *d* orbitals sufficiently to enable good orbital overlap.[16] However, as π overlap occurs off the bond axis, the shrinkage needed is not too great. The involvement of *d* orbitals in bonding can qualitatively explain large angles, but it is difficult to confirm the bond shortening in the absence of an independent standard. For the gallium compounds, where Ga has a filled 3*d* shell, participation of the 4*d* orbitals would need to be invoked, but there is no way of knowing how large the energy mismatch would be. Similarly, Fe^{3+} has a d^5 configuration with each 3*d* orbital already singly occupied (high spin) so that (*d–p*) π overlap is perhaps questionable in this case.

Table 13. X–O–X Angles (°) for iron, gallium, and aluminium systems

Compound	Ref.	Angles
$Na_4Fe_2O_5$	11, *a*	125.3, 169.5, 125.4
$Na_{14}Fe_6O_{16}$	*b*	124.0, 123.8, 133.2, 168.0
$K_6Fe_2O_6$	13	88.6
$Na_8Fe_2O_7$	*c*	119.7
$LiGaO_2$	*d*	116.1, 114.0
$Na_8Ga_2O_7$	*e*	120.06
γ-$LiAlO_2$	*f*	124.6
$CaAl_2O_4$	*g*	132, 120
$Na_7Al_3O_8$		130.1, 136.9, 145.4, 157.1
$Na_{17}Al_5O_{16}$	7	159.5, 173
Ca_2FeAlO_5	*h*	130.8
$Ca_2Fe_{1.43}Al_{0.57}O_5$ $Ca_2Fe_{1.28}Al_{0.72}O_5$	} *i*	128.4

[a] G. Brachtel and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1978, **446**, 97. [b] G. Brachtel and R. Hoppe, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 43; *Z. Anorg. Allg. Chem.*, 1978, **446**, 87. [c] G. Brachtel and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1978, **438**, 15. [d] M. Marezio, *Acta Crystallogr.*, 1965, **18**, 481. [e] D. Fink and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1976, **122**, 1. [f] M. Merezio, *Acta Crystallogr.*, 1965, **19**, 396. [g] M. W. Dougill, *Nature (London)*, 1957, **180**, 292. [h] A. A. Colville and S. Geller, *Acta Crystallogr., Sect. B*, 1971, **27**, 2311. [i] A. A. Colville and S. Geller, *Acta Crystallogr., Sect. B*, 1972, **28**, 3196.

For a comprehensive review of bonding in silicates the reader is referred to a review by Dent Glasser.[17]

The effect of the Na^+ ions in the structure cannot, however, be ignored. In the structure of rosenhahnite, $Ca_3Si_3O_8(OH)_2$, in which isolated $Si_3O_8(OH)_2$ groups are surrounded by Ca^{2+} ions, the asymmetric field generated by the cations causes angle distortions which also lead to bond-length changes.[18] The aluminates described in this paper would be expected to provide further data for comparison of the various bonding theories and we have therefore examined the bond-angle and bond-length data of these compounds. The hybridisation state of the oxygen in the Al–O bond in the Al–O–Al linkage

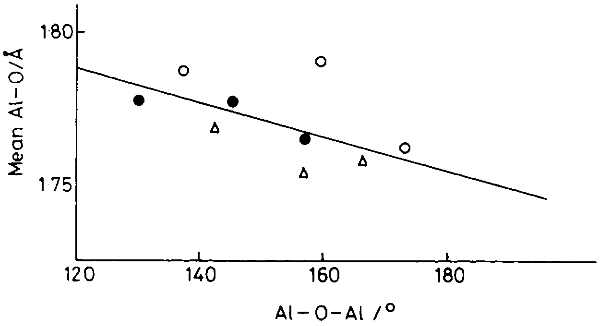

Figure 4. Plot of mean Al–O bond length *versus* Al–O–Al angle for $Na_7Al_3O_8$ (●), $Na_{17}Al_5O_{16}$ (○), and $Ca_{8.5}NaAl_6O_{18}$ [19] (△)

has been used to explain the variations in the Al–O–Al angle. If the angle is near to 120° then the hybridisation state is sp^2, whereas at 180° it is clearly sp. For the sp^2 state the third hybrid orbital is σ-bonded to the alkali-metal atom and thus the s character of this bond will affect the Na–O bond length (A–O) and the Al–O–Al angle (T–O–T). Brown *et al.*[19] have studied the correlation between the A–O, T–O lengths and T–O–T angles for a variety of aluminosilicates and observed a negative correlation between T–O and A–O and a positive correlation between A–O and T–O–T. We found no such correlations for the sodium aluminates reported in this paper, which suggests that the strength of the Na–O interaction is not a significant factor. In an analysis of the structure of $Ca_{8.5}NaAl_6O_{18}$, Nishi and Takeuchi [20] observed a dependence of the Al–O–Al bridge bond lengths on the angles at oxygen. A plot of these data gave a slope consistent with that obtained by Brown *et al.* for the Al–O bond *versus* the Al–O–Si angle. Extrapolation of the line gave A–O 1.74 Å at Al–O–Al 180° and 1.77 Å at 120°. This was taken to be consistent with the d-p_π model of bonding proposed by Cruickshank.[21] Data obtained from $Na_7Al_3O_8$ and $Na_{17}Al_5O_{16}$ also showed a good correlation with the data of Nishi and Takeuchi (Figure 4), although there was much poorer agreement for a plot of the Al–O bond length against the mean of the three angles involving that bond.

In conclusion we feel that our results indicate that d-p_π bonding in aluminates occurs to a lesser degree than that in silicates and that the observed distortions from the tetrahedral angles are more likely to be the result of the asymmetric cation field of the Na^+ ions.

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