

The Al_6O_{18} Rings of Tetrahedra in the Structure of $\text{Ca}_{8.5}\text{NaAl}_6\text{O}_{18}$

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The orthorhombic unit cell of $\text{Ca}_{8.5}\text{NaAl}_6\text{O}_{18}$ has dimensions $a=10.875$ (3), $b=10.859$ (3), $c=15.105$ (10) Å, and space group $Pbca$; $Z=4$, $D_x=3.028$ g cm⁻³. In the structure, six AlO_4 tetrahedra are joined, sharing corners, to form an Al_6O_{18} ring. The Al's are distributed at positions very near the corners of the pseudo-cubic subcells [$\mathbf{a}'=(\mathbf{a}+\mathbf{b})/4$, $\mathbf{b}'=(-\mathbf{a}+\mathbf{b})/4$, $\mathbf{c}'=\mathbf{c}/4$]. The Ca's are at positions near the remaining corners and body centres of the subcells. The Al–O bond lengths vary from 1.722 (4) to 1.770 (4) Å, giving a mean value of 1.751 (1) Å. The Al–O bond length decreases with increasing Al–O–Al angle; extrapolation of the correlation line gives Al–O=1.747 Å at Al–O–Al=180°, and 1.778 Å at 120°. The Ca's are irregularly coordinated by oxygen atoms; observed coordination numbers are 6, 7 and 8. One of the five non-equivalent Ca's is split into two half atoms separated by 0.556 (3) Å. The Na's are partly distributed over a set of the Ca positions substituting for the Ca's with the Na:Ca ratio of 0.33 (2), and partly at the centre of the tetrahedral ring with occupancy 0.50 (2).

Introduction

X-ray emission spectroscopy on $\text{Ca}_9\text{Al}_6\text{O}_{18}$ (Day, 1963) suggests that the Al is in tetrahedral coordination in the crystalline phases of the $\text{Ca}_9\text{Al}_6\text{O}_{18}$ – Na_2O solid solution occurring in Portland cement clinker. Since the Al:O ratio of this series of compounds is 1:3, the AlO_4 tetrahedra in their structures must be joined to form a certain type of aluminate radical. Moore (1967) and Maki & Sugimura (1970) have in fact postulated the existence of a ring consisting of six AlO_4 tetrahedra. It is anticipated that structural studies on this solution series will elucidate experimentally the nature of pure Al–O tetrahedral bonds which have so far been studied mainly in the states affected by Si in the Si–O–Al linkages of mineral structures. The solid solution series is thus of particular interest not only in its obvious importance in cement chemistry but also in mineral chemistry. We have therefore undertaken crystallochemical studies on this series. The present paper reports the crystal structure of the orthorhombic phase, which we have determined before other phases. Though we have been informed that the structure of the cubic phase, $\text{Ca}_9\text{Al}_6\text{O}_{18}$, has been determined in Professor J. W. Jeffery's laboratory, no details have been made available to us. The cubic phase has also been studied in Professor S. Iwai's laboratory (Iwai, 1974).

Experimental

Orthorhombic crystals of composition $\text{Ca}_{8.5}\text{NaAl}_6\text{O}_{18}$ were kindly supplied by Dr I. Maki. Accounts have appeared on the method of preparation, and on the morphology of the crystals (Maki, 1973, 1974). Crystals are frequently twinned on {110}. Using a piece of crystal of irregular shape with maximum dimension 0.175 mm, we determined, with a four-circle diffractometer (Mo $K\alpha$, $\lambda=0.71069$ Å), the following cell dimensions: $a=10.875$ (3), $b=10.859$ (3), $c=15.105$ (10) Å. The

unit cell contains four formula units, the calculated density being 3.028 g cm⁻³.

X-ray photographs revealed a marked substructure; reflexions are in general very strong if h , k , and l are multiples of four. The axes of the subcell, \mathbf{a}' , \mathbf{b}' , and \mathbf{c}' , are related to those of the original cell as follows: $\mathbf{a}'=(\mathbf{a}+\mathbf{b})/4$, $\mathbf{b}'=(-\mathbf{a}+\mathbf{b})/4$, $\mathbf{c}'=\mathbf{c}/4$. The extinction rule is consistent with that of the space group $Pbca$; $hk0$, $h0l$, and $0kl$ reflexions are respectively missing if $h \neq 2n$, $l \neq 2n$, and $k \neq 2n$. The above crystal data agree well with those reported by Maki (1973).

While selecting crystals by X-rays, we came across a crystal piece which exhibited absences consistent only with $P2_12_12_1$. The crystal had the approximate shape of a pentagonal plate parallel to (001) with a thickness of 0.1 mm; the five edges measured 0.1, 0.15, 0.1, 0.15 and 0.2 mm. This crystal was later found to be a twin, in which individuals A and B , with different volumes, are twinned on (110). Since they have, as shown above, a very strong tetragonal pseudo-symmetry, the hkl reflexions of A and khl reflexions of B are superposed to give a composite reciprocal lattice, simulating that of a crystal with space group $P2_12_12_1$. The lattice constants determined for this crystal are:

$$a=10.868$$
 (2), $b=10.856$ (2), $c=15.128$ (8) Å.

These cell dimensions give a calculated density of 3.026 g cm⁻³.

Intensity data

The ω – 2θ scan technique was used, for the first crystal, to measure one octant (to 80° in 2θ) of Mo $K\alpha$ intensity data. Since reflexions were mostly weak, a slow scan speed of 1° (2θ) min⁻¹ was applied. Out of 5519 reflexions measured, only 2210 had intensities higher than the cut-off level of 3 c.p.s. Intensities were then corrected for Lorentz and polarization factors. Correction for transmission was made ($\mu=28.0$ cm⁻¹) by approximating the crystal shape to that of a poly-

hedron. This correction was in fact made at the final stage of the structure refinement. We then noticed that the effect of the correction was negligible. The correction was therefore not applied for the second crystal.

The intensities from the second crystal, the twin composite, were measured in a similar way, but in this case up to 60° in 2θ and with a slower scan speed of $0.5^\circ (2\theta) \text{ min}^{-1}$. The cut-off level was likewise set at 3 c.p.s. Out of 2971 reflexions measured, 1842 had intensities higher than this level.

Determination and refinement of the structure

The structure analysis was carried out based on the intensity data from the first crystal. Though the existence of the strong substructure did not permit straightforward determination of the structure, it in turn aided in locating cations from consideration of the Patterson synthesis. In addition to the space-group extinctions, all reflexions are missing or very weak if $h+k \neq 2n$, suggesting the existence of a pseudo translation of $(\mathbf{a} + \mathbf{b})/2$. These considerations permitted the construction of a structural model based on rings formed by six AlO_4 tetrahedra; the Al's being located near the corners of subcells with 36 instead of 38 cations at or near the remaining corners and body centres. In the course of refining the structure to $R = 15.3\%$, there was evidence that the Na's were partly located at the Ca(5) position and partly at the origin. The structure was then refined, with the full-matrix least-squares program *ORFLS* (Busing, Martin & Levy, 1962) to $R = 7.4\%$ ($R_w = 10.6\%$) for 2006 reflexions, those obviously affected by extinction and those having values smaller than $2\sigma(I)$ being omitted. When we applied isotropic temperature factors, the final value of R was 9.7% ($R_w = 13.0\%$). An empirical weighting factor was used of the form $w = 1/(a + F_{\text{obs}} + cF_{\text{obs}}^2)$ (Cruickshank, 1965) with $a = 20$ and $c = 0.01157$. The maximum and average shifts of atomic coordinates as fractions of

the e.s.d.'s in the final cycle of computations are respectively 0.18 and 0.03. The atomic scattering curves were constructed from data provided by *International Tables for X-ray Crystallography* (1962).

Another refinement of the structure was carried out based on intensities from the twin composite. Since in an early stage we misconceived it to be a distinct phase having space group $P2_12_12_1$, we failed to refine the structure; the value of R could not be reduced to less than 13.8% ($R_w = 19.9\%$), and unusual Al-O bond lengths of 1.88 and 1.65 Å were, for example, obtained. The volume ratio of the individuals *A* and *B* was readily estimated to be 1:0.281 (7) on the basis of the intensities of $h0l$ (or $0kl$) reflexions of one individual that superpose with $0kl$ (or $h0l$) reflexions of the other, which are necessarily missing due to the space group extinction of *Pbca*. Using this ratio, we separated, with a computer program, the composite intensity of each multiple reflexion to give a set of intensity data from *A*. Leaving out substructure reflexions and $|F_o|$'s < 15.5

Table 1. Fractional atomic coordinates ($\times 10^5$)

| | x | y | z |
|-------|-------------|-------------|-------------|
| Ca(1) | 268 (26) | 196 (19) | 51825 (11) |
| Ca(2) | -394 (11) | 1771 (7) | 23927 (5) |
| Ca(3) | 928 (10) | 26744 (8) | 13313 (6) |
| Ca(4) | 25648 (13) | 27066 (8) | 25278 (8) |
| Ca(5) | 26267 (12) | 24622 (13) | 49832 (9) |
| Na | 0 | 0 | 0 |
| Al(1) | -482 (15) | -21407 (11) | 11603 (8) |
| Al(2) | 23755 (14) | -327 (14) | 11292 (10) |
| Al(3) | 24208 (14) | 543 (13) | -10861 (9) |
| O(1) | -14416 (39) | -13388 (37) | 10911 (29) |
| O(2) | 11066 (40) | -10125 (41) | 12634 (27) |
| O(3) | 28698 (34) | -2208 (30) | 229 (24) |
| O(4) | -730 (53) | -28562 (32) | 21778 (22) |
| O(5) | 1956 (42) | -29335 (32) | 1724 (22) |
| O(6) | 35529 (36) | -7220 (35) | 17361 (24) |
| O(7) | 18863 (35) | 14794 (34) | 13240 (27) |
| O(8) | 16233 (35) | -12774 (31) | -14188 (25) |
| O(9) | 37170 (33) | 6610 (23) | -15970 (23) |

Table 2. Thermal parameters ($\times 10^5$)

The expression used for the anisotropic thermal parameters was $\exp \{ -(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{33}kl) \}$.

| | β_{11} | β_{22} | β_{33} | β_{12} | β_{13} | β_{23} |
|-------|--------------|--------------|--------------|--------------|--------------|--------------|
| Ca(1) | 129 (12) | 103 (11) | 222 (14) | 20 (13) | 7 (14) | 0 (11) |
| Ca(2) | 204 (7) | 129 (5) | 58 (3) | 36 (7) | 5 (6) | -2 (3) |
| Ca(3) | 163 (7) | 179 (6) | 54 (3) | 20 (7) | -12 (5) | 41 (4) |
| Ca(4) | 451 (9) | 131 (6) | 68 (3) | 51 (7) | -87 (5) | 12 (6) |
| Ca(5) | 256 (9) | 228 (7) | 91 (4) | 2 (8) | 9 (5) | -6 (4) |
| Na | 359 (62) | 928 (81) | 290 (30) | -388 (79) | -170 (46) | 456 (42) |
| Al(1) | 109 (10) | 93 (8) | 30 (4) | -21 (10) | -12 (7) | -4 (5) |
| Al(2) | 103 (11) | 142 (14) | 80 (7) | -35 (9) | 0 (7) | 6 (7) |
| Al(3) | 84 (10) | 88 (12) | 33 (6) | -16 (8) | -4 (7) | -36 (6) |
| O(1) | 265 (33) | 295 (32) | 246 (19) | 138 (27) | -80 (21) | -32 (21) |
| O(2) | 350 (35) | 462 (37) | 164 (16) | -256 (30) | 79 (20) | -116 (22) |
| O(3) | 214 (29) | 274 (32) | 57 (12) | -71 (22) | 29 (16) | 27 (20) |
| O(4) | 794 (46) | 197 (26) | 61 (13) | 61 (35) | -2 (24) | -3 (15) |
| O(5) | 525 (42) | 204 (25) | 60 (13) | -37 (27) | 34 (19) | -19 (15) |
| O(6) | 248 (30) | 216 (31) | 119 (14) | 25 (23) | -113 (17) | -39 (17) |
| O(7) | 231 (32) | 267 (32) | 161 (17) | 168 (24) | -91 (19) | -29 (19) |
| O(8) | 252 (30) | 145 (27) | 139 (15) | -42 (22) | -4 (18) | -69 (16) |
| O(9) | 228 (30) | 124 (28) | 117 (14) | -88 (21) | 12 (16) | 30 (16) |

which roughly corresponds to $3\sigma(I)$, a total of 1223 F_o 's were then used to refine the structure. Starting with the atomic coordinates obtained from the first crystal, least-squares calculations were performed in a way similar to that described above, giving with isotropic temperature factors the final value of $R=7.3\%$ ($R_w=9.6\%$), and with anisotropic thermal parameters $R=3.5\%$ ($R_w=4.7\%$). The average and maximum shifts of atomic coordinates as fractions of e.s.d.'s in the final cycle of computations are respectively 0.10 and 0.53.

The atomic coordinates obtained from the second crystal are given in Table 1, and thermal parameters in Table 2. Bond lengths and angles mentioned in the

Discussion are those based on the atomic coordinates from the second crystal, unless otherwise indicated.*

Discussion

The Ca's and Al's are distributed in the structure at positions very near the corners and body centres of the pseudocubic subcells. Six tetrahedra are joined, as

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30811 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. Bond lengths (Å) and estimated valence sums (v. u.)

Valence sums have been calculated with a program by Professor G. Donnay.

| | Ca(1) | Ca(2) | Ca(3) | Ca(4) | Ca(5) | Al(1) | Al(2) | Al(3) | Na | Valence sum |
|------|----------------------------------|----------------|----------------|----------------------------------|----------------------------------|----------------|----------------|----------------|--------------------|-------------|
| O(1) | | 2.983 0.102 | | 2.630 0.231 | 2.447 0.325 | 1.751 0.740 | | 1.755 0.751 | 2.700 × 2 0.078 | 2.226 |
| O(2) | | 2.476 0.296 | | 2.770 0.179 | 2.849 0.150 | 1.761 0.725 | 1.754 0.750 | | 2.510 × 2 0.168 | 2.268 |
| O(3) | 2.311 0.198 2.381 0.178 | | | | 3.008 0.085 2.494 0.299 | | 1.767 0.731 | 1.770 0.728 | 3.130 × 2 0.000 | 2.220 |
| O(4) | | 2.235 0.427 | 2.325 0.345 | 2.845 0.151 2.813 0.163 | | 1.722 0.783 | | | | 1.868 |
| O(5) | 2.299 0.202 2.273 0.211 | | 2.310 0.350 | | 2.440 0.329 | 1.743 0.752 | | | | 1.845 |
| O(6) | 2.911 0.067 | 2.242 0.423 | 2.361 0.331 | 2.412 0.326 | | | 1.744 0.765 | | | 1.911 |
| O(7) | | 2.999 0.096 | 2.343 0.338 | 2.372 0.349 | 2.464 0.315 | | 1.751 0.754 | | | 1.852 |
| O(8) | | 2.561 0.262 | 2.409 0.313 | 2.392 0.337 | 2.609 0.246 | | | 1.760 0.743 | 3.104 × 2 0.004 | 1.906 |
| O(9) | 2.661 0.116 3.105 0.028 | 2.286 0.394 | 2.381 0.323 | 2.542 0.265 | | | | 1.737 0.778 | | 1.904 |
| Mean | 2.563 | 2.540 | 2.355 | 2.597 | 2.616 | 1.744 | 1.754 | 1.755 | 2.861 | |

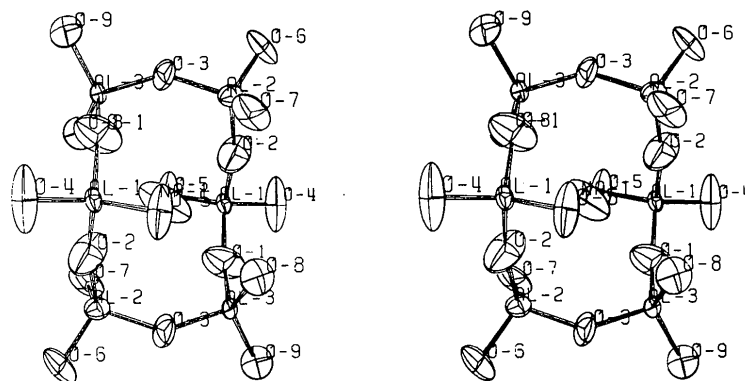


Fig. 1. Stereoscopic drawing of the Al_6O_{18} tetrahedral ring with Na at its centre, viewed along the b axis, the a and c axes being respectively parallel to the vertical and horizontal directions.

postulated by Moore (1967), to form an Al_6O_{18} ring (Fig. 1) with a pseudo-threefold axis through the origin and the point $0, \frac{1}{2}, \frac{1}{4}$. The direction of this axis corresponds to that of the body diagonal of the cubic cell of $\text{Ca}_9\text{Al}_6\text{O}_{18}$, which is conventionally abbreviated to C_3A in cement chemistry. The configuration of the ring may be regarded as a distorted version of the unit ring in the tridymite structure; with respect to the pseudo-threefold axis, the apices are alternately pointing in one direction and the other. The arrangement of the rings in the unit cell is shown in Fig. 2.

The Al-O bond lengths (\AA) are: overall mean 1.751 (1) [1.752 (2)]; mean of the bridge bonds 1.760 (2) [1.759 (2)]; mean of the non-bridge bonds 1.743 (2) [1.745 (2)]. In the above, the bond lengths obtained from the first crystal free from twinning are given in brackets for comparison. The overall mean value agrees well with that of Al-O, 1.75 \AA , the use of which has been recommended by Smith & Bailey (1963) for framework structures. A marked feature is the dependence of Al-O-Al bridge bond lengths on the angles at O. For each Al-O-Al link, the mean length (\AA) of the two bridge bonds and the angle ($^\circ$) at O are listed below.

| | Mean length | Angle at O |
|-------------------|-----------------------|-----------------------|
| Al(2)-O(3)-Al(3) | 1.769 (3) [1.766 (4)] | 142.3 (2) [142.6 (3)] |
| Al(1)-O(1)-Al(3') | 1.753 (3) [1.759 (4)] | 157.0 (3) [155.9 (3)] |
| Al(1)-O(2)-Al(2) | 1.758 (3) [1.754 (4)] | 166.5 (3) [166.0 (3)] |

The values in brackets are those from the first crystal. Though these data are limited in number and we should perhaps await the result of our work on the structure of the monoclinic phase, they are plotted in Fig. 3. The data give in the diagram a slope of -0.0005_2 , which is to be compared with the slope of -0.0006 (2) given by Brown, Gibbs & Ribbe (1969) for the Al-O bond *versus* the Al-O-Si angle in framework structures. Our line is extrapolated to give Al-O = 1.74, \AA at Al-O-Al = 180° , and 1.77 $_8$ \AA at 120° . The above trend in the nature of the Al-O bonds is quite similar to that of Si-O bonds and is consistent with Cruickshank's (1961) *d-p* π -bond model. The individual bond lengths and valence sums at O's are given in Table 3, and O-O distances and angles at Al's are in Table 4. The valence sums were calculated with the techniques developed by Donnay & Allmann (1970).

The above relation between Al-O bridge bonds and angles at the bridge oxygen atoms should be compared with those in the structures of $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ (Bartl & Scheller, 1970) and $11\text{Ca} \cdot 07\text{Al}_2\text{O}_3 \cdot \text{CaF}_2$ (Williams, 1973). These two structures are isotypic and consist of links of AlO_4 tetrahedra; they have a mean length of 1.76 \AA for Al-O bridge bonds, and a mean value of 137.3° for the angles at the bridge oxygen atoms. These values do not agree well with those expected from the broken line shown in Fig. 3.

The tetrahedral rings are held together by Ca atoms to form the structure. Among the Ca's, Ca(3) is co-

Table 4. O(*p*)-Al(*q*)-O(*r*) angles ($^\circ$) and O(*p*)-O(*r*) distances (\AA)

| <i>p</i> | <i>q</i> | <i>r</i> | Angle | Distance |
|----------|----------|----------|-----------|-----------|
| 1 | 1 | 2 | 106.0 (2) | 2.806 (6) |
| | | 4 | 105.3 (2) | 2.761 (6) |
| | | 5 | 109.0 (2) | 2.845 (6) |
| 2 | 4 | 4 | 104.2 (2) | 2.750 (6) |
| | | 5 | 108.1 (2) | 2.837 (5) |
| 4 | 5 | 2 | 122.9 (2) | 3.044 (5) |
| | | 2 | 106.2 (2) | 2.815 (5) |
| 2 | 2 | 3 | 104.9 (2) | 2.773 (6) |
| | | 7 | 108.1 (2) | 2.837 (6) |
| | | 6 | 103.0 (2) | 2.747 (5) |
| 3 | 7 | 6 | 111.1 (2) | 2.901 (5) |
| | | 7 | 122.5 (2) | 3.064 (5) |
| 6 | 7 | 3 | 107.8 (2) | 2.848 (5) |
| | | 3 | 105.5 (2) | 2.810 (5) |
| 3 | 3 | 1' | 105.1 (2) | 2.784 (5) |
| | | 8 | 110.7 (2) | 2.891 (5) |
| 1' | 8 | 9 | 100.9 (2) | 2.692 (6) |
| | | 9 | 125.8 (2) | 3.115 (5) |

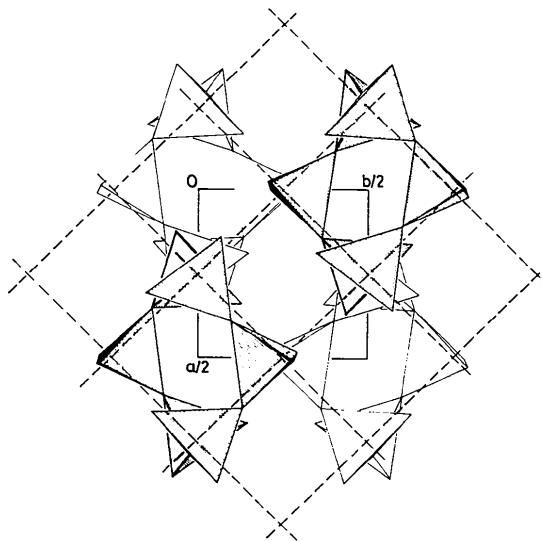


Fig. 2. The *c* axis projection of the structure, showing tetrahedral rings; $\frac{1}{2}$ cell is outlined by heavy lines, subcells by broken lines. The rings at the $\frac{1}{2}$ level are stippled, while those at the zero level are shown by plain tetrahedra.

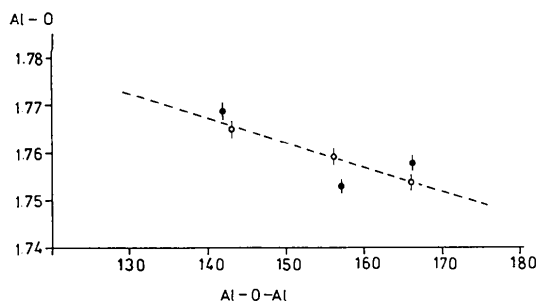


Fig. 3. Variation of the Al-O bond length (\AA) *versus* the Al-O-Al angle ($^\circ$); open circles from the first crystal and the solid circles from the second.

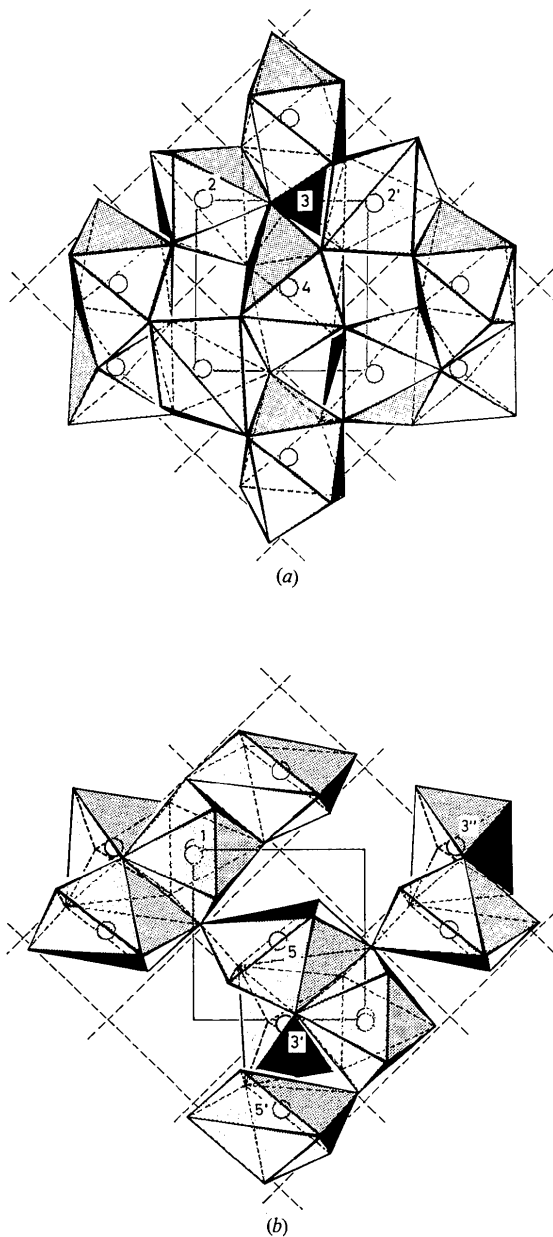


Fig. 4. The *c*-axis projection of the structure, showing polyhedra about Ca's which are approximately in the slabs bounded by (a) $z=0$ and 0.25 , (b) $z=0.25$ and 0.50 ; $\frac{1}{4}$ cells and subcells are shown as in Fig. 2. Numbers correspond to the notation of atoms given in Table 1. When the notation of the atom is associated with a prime or double prime, the atom is derived from the equivalent atom at x, y, z (as given in Table 1) by the following symmetry operations: $2'$ inversion at $0, 0, \frac{1}{2}$ followed by glide c at $x, \frac{1}{2}, z$; $3'$ glide a at $x, y, \frac{1}{2}$; $3''$ glide a at $x, y, \frac{1}{2}$ followed by glide b at $\frac{1}{2}, y, z$; $5'$ inversion at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ followed by glide b at $\frac{1}{2}, y, z$.

ordinated by six oxygen atoms, but others are irregularly coordinated by seven or eight oxygen atoms (Fig. 4), giving a mean Ca–O bond length of 2.534 \AA . The separation of the split Ca(1) is found to be $0.556 (3) \text{ \AA}$. It is to be noted that there are altogether 36 available locations for the 34 Ca atoms in the unit cell. It is notable that the excess locations are preferably distributed in the set of Ca(5) positions to accommodate two of the four Na's per cell. The Na:Ca ratio in the positions has in fact been calculated to be $0.33 (2)$. The remaining two Na's are located, with occupancies of $0.50 (2)$, at the centres of the tetrahedral rings. The thermal ellipsoids of this particular set of Na's (Fig. 1) may suggest, by analogy with the Na's in the structure of zeolite type A (Howell, 1960), a statistical distribution over positions slightly off the centre.

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