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The Crystal Structure of Tricalcium Aluminate, $Ca_3Al_2O_6$*

BY P. MONDAL† AND J. W. JEFFERY

Department of Crystallography, Birkbeck College, London University, Malet Street, London WC1E 7HX, England

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The structure of tricalcium aluminate, $Ca_9Al_6O_{18}$, has been determined after 12 trials. There are 24 possible arrangements of the cations arising from space group and Patterson synthesis considerations. The twelfth trial gave reasonable oxygen positions on a partial Fourier map and refined by a full-matrix least-squares program to $R=5{\cdot}1\%$. The intensity data were collected by photometry of integrated Weissenberg photographs. The space group is *Pa*3 and $a=15{\cdot}263$ Å. The structure consists of rings of six AlO_4 tetrahedra (Al_6O_{18}) eight to a unit cell, surrounding holes of radius 1·47 Å at $\frac{1}{8}\frac{1}{8}\frac{1}{8}$ and its symmetry-related positions, with Ca^{2+} ions holding the rings together. The Ca coordination polyhedra have marked departures from regular octahedra, but the AlO_4 tetrahedra are much less distorted. The relation of the structure to the reactivity of tricalcium aluminate in Portland cement is discussed, as well as the alteration in properties and structure with replacement of Ca^{2+} by $2Na^+$ in a solid solution series. Suggestions are made for the structure of the isomorphous $Na_8Ca_2Si_6O_{18}$, which almost certainly has sixfold rings of SiO_4 tetrahedra.

Introduction

The compound tricalcium aluminate, $Ca_3Al_2O_6(3CaO.Al_2O_3\equiv C_3A$ in cement chemistry symbols‡) in an impure form, is one of the main components of Portland cement. In the form found in cement clinker a small proportion of Al ions are sometimes replaced by other ions such as Fe^{3+} and Ca ions may be replaced by Mg^{2+}, $2Na^+$ or $2K^+$. Ground Portland cement clinker reacts very quickly with water to form a congealed mass. This phenomenon is known as 'flash set' and is attributed to the high reactivity of C_3A (present in the clinker) with water. 'Flash set' is avoided by grinding a carefully adjusted amount (2%–5%) of gypsum ($CaSO_4.2H_2O$), along with the Portland cement clinker. Other substances such as $CaCl_2$, $Ca(NO_3)_2$, CaI_2, also act as retarders (Forsén, 1938). The mechanism by which these chemicals affect the reactivity of C_3A is not known, although an extensive investigation of the effect has been carried out by Gupta, Chatterji & Jeffery (1970–73). An accurate crystal structure determination of C_3A was therefore required to reveal any structural reasons for high reactivity and any blocking mechanisms which might account for the retardation phenomena.

The determination of the structure of C_3A has been attempted previously by a number of investigators – Steele & Davey (1929), Büssem (1938), McMurdie (1941), Ordway (1952) and Moore (1966).

Steele & Davey (1929) made an X-ray investigation of C_3A based on powder diagrams and obtained a cubic unit cell with $a=7{\cdot}626$ Å and probable space group *Pm*3*m*. Their proposed structure contained AlO_6 octahedra and nearly square planar AlO_4 groups.

Büssem (1938) observed the similarity of the X-ray powder diffraction patterns of C_3A and perovskite ($CaTiO_3$, $a=3{\cdot}8$ Å) and proposed a space group *Pa*3 with $a=15{\cdot}22$ Å $(=4\times3{\cdot}8)$ Å for C_3A. He derived a tentative structure of C_3A as a polyhedron network of AlO_6, AlO_4 and CaO_6. In this model nine oxygen atoms were found in the neighbourhood of each of the calcium atoms situated at $\frac{1}{8}\frac{1}{8}\frac{1}{8}, \frac{3}{8}\frac{3}{8}\frac{3}{8}, \frac{3}{8}\frac{3}{8}\frac{1}{8}, \frac{3}{8}\frac{1}{8}\frac{1}{8}$, together with their symmetry-related positions of the space group *Pa*3. Six oxygen atoms out of the nine lie on a planar ring about these calcium atoms and the other three oxygen atoms are on one side of the planar arrangement. This unusual coordination also produced a square planar arrangement of oxygen atoms round the Al atoms at $\frac{1}{4}\frac{1}{4}0$ and its symmetry-related positions.

McMurdie (1941) proposed that C_3A may have a structure with Ca and Al at or near the centres and corners of 3·8 Å cubes but was unable to predict the arrangement of oxygen atoms.

Ordway (1952) confirmed the unit-cell parameter $a=15{\cdot}22$ Å, and space group *Pa*3 for C_3A. He attempted to solve the structure of C_3A using two-dimensional data obtained from a synthetically grown single crystal. He was, however, unable to reconcile his two-dimensional X-ray intensity data with the structural model proposed by Büssem, or to find a model consistent with his data.

Moore (1966) proposed a structure of C_3A based on Al_6O_{18} rings of six tetrahedra, with the same arrangements of Ca and Al as those obtained by McMurdie (1941). Such rings do, in fact, occur in C_3A but the relation to the Ca atoms was incorrect and the structure could not be reconciled with the intensity data.

* The main part of this paper is a modified form of the Ph. D. thesis submitted by P. Mondal to London University.

† Present address: Department of Physics, The University, York, England.

‡ C≡CaO; A≡Al_2O_3; F≡Fe_2O_3; S≡SiO_2; N≡Na_2O; H≡H_2O.

Experimental

Ordway (1952) suggested that a crystal of C_3A can be grown from a melt whose composition lies in the range of 59% CaO–41% Al_2O_3 to 50% CaO–50% Al_2O_3 by weight. However, the phase diagram given by Nurse, Welch & Majumdar (1965) shows that C_3A without admixture can only be grown at about 1540 °C from a melt with composition in the range 57% CaO–43% Al_2O_3 to 50% CaO–50% Al_2O_3. With higher proportions of CaO, the initial products will be CaO followed by C_3A; below the 50/50% point C_3A is accompanied by CA (or $C_{12}A_7$ in air of normal humidity). This narrower range was confirmed by the present investigation. An attempt to grow C_3A crystals from a melt with composition 59% CaO and 41% Al_2O_3 by weight using the Griffin–Telin hot stage microscope always led to small cubic crystals of CaO attached to the C_3A octahedra. A 55/45% mixture was finally used. This melted into a homogeneous liquid at 1539 ± 5 °C, and on sudden chilling produced only microcrystals of C_3A. The temperature was slowly raised until all but one of these microcrystals were melted and this seed was grown to the appropriate size by slow cooling. The sample was then suddenly quenched and the surrounding liquid phase immediately solidified into glass. The glass was removed and the C_3A crystal ground into a sphere using a modified Schuyff and Hulscher apparatus (Jeffery, 1971).

From a mixture of 57% CaO and 43% Al_2O_3, 43% at most can be crystallized as a single crystal before CA starts to crystallize. The mixture actually used (55/45%) can yield up to 41% as a single crystal of C_3A.

A randomly oriented spherical crystal mounted on the end of a hollow borosilicate glass fibre was approximately set along a cube axis as the rotation axis using the method described by Jeffery (1949). The mean radius of the crystal and its standard deviation were obtained from shadow photographs (Jeffery, 1971). The accurate cell parameter was determined by a back-reflexion technique similar to that described by Farquhar & Lipson (1946). The density of a C_3A crystal was determined by a flotation method. The Laue symmetry and space group of C_3A were confirmed by oscillation, Laue, Weissenberg and precession methods. The rotation, Weissenberg and precession photographs about the c axis showed that intense reflexions were only present on zero and $4n$ layers and that hkl reflexions were very strong when $h+k+l=8n$ and h, k and $l=4n$. Hence C_3A has a body-centred pseudo-cell with $a'=\frac{1}{4}a$. This is confirmed by the powder diffraction data, where the strong lines all correspond to the pseudo-cell, except for one low-angle line, and there is only one strong line (also at a low angle) which does not correspond to body centring of the pseudo-cell. An $h0l$ level precession photograph taken with Nb-filtered Mo K radiation is shown in Fig. 1.

Three-dimensional X-ray intensity data from the spherical crystal mounted about a cube axis (taken as c) were collected on a Nonius integrating Weissenberg camera (Wiebenga & Smits, 1960) which was checked and adjusted as described by Jeffery (1971). The camera was aligned relative to the X-ray tube by the method described by Whitaker (1965). With the equi-inclination

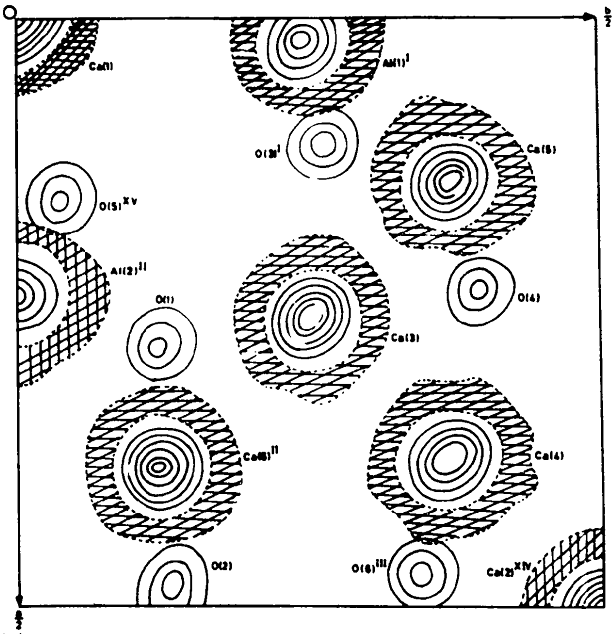


Fig. 2. Composite Fourier diagram through atom peaks. The contouring is at intervals of 100 e Å^{-3} round the Ca and Al atoms and 50 e Å^{-3} round the oxygen atoms. Labelling as in Table 3.

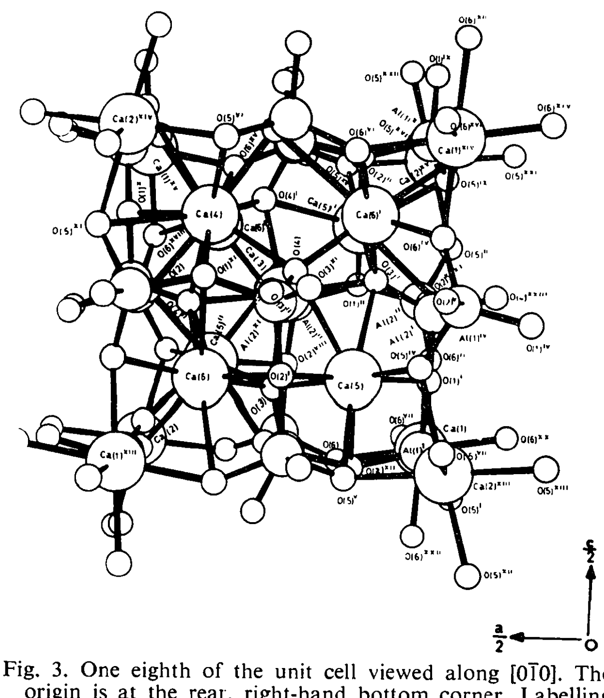


Fig. 3. One eighth of the unit cell viewed along [0$\bar{1}$0]. The origin is at the rear, right-hand bottom corner. Labelling as in Table 3.

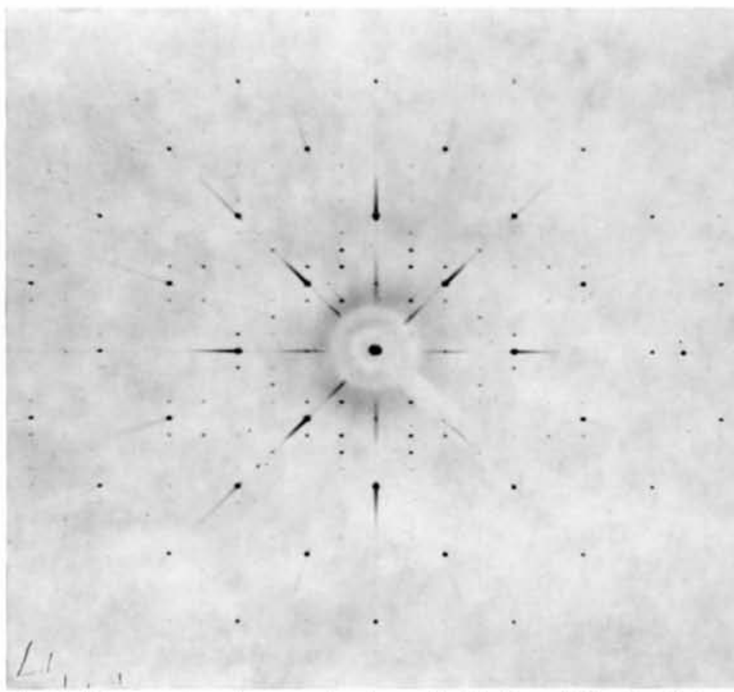


Fig. 1. *h0l* precession photograph taken with Nb-filtered Mo *K* radiation.

Weissenberg technique, 0–14 levels could be photographed with Cu $K\alpha$ radiation and a maximum equi-inclination angle $\mu=45°$, but only 0–11 layers of Weissenberg photographs were collected. Reflexions $hk12$ to $hk14$ were already recorded on the 0–11 layers because of the threefold symmetry axis in the crystal. In order to avoid the effect of systematic multiple reflexion the camera equi-inclination angle was deliberately mis-set by 0·5° for all even upper-layer photographs.

The optical densities of the integrated Weissenberg films were measured with a special photometer designed by Jeffery (1963), except that densities less than 0·05 were measured visually from non-integrated films. The weight for each individual X-ray reflexion was calculated on the basis of the method developed by Jeffery & Rose (1964). The raw intensity data were corrected for Lorentz–polarization and absorption factors. The multiple-film correlation factors of individual layers were obtained by a least-squares method (Hamilton, Rollett & Sparks, 1965). Weighted average intensities of equivalent reflexions in a layer and a combined weight were calculated to produce a set of hkl data from $\frac{1}{8}$ of reciprocal space. From threefold symmetry-related reflexions a unique correlated set of hkl data was obtained for $\frac{1}{24}$ of reciprocal space by using a modification of the method of Hamilton, Rollett & Sparks (1965). 6850 reflexions were measured and these reduced to 1191 non-equivalent reflexions.

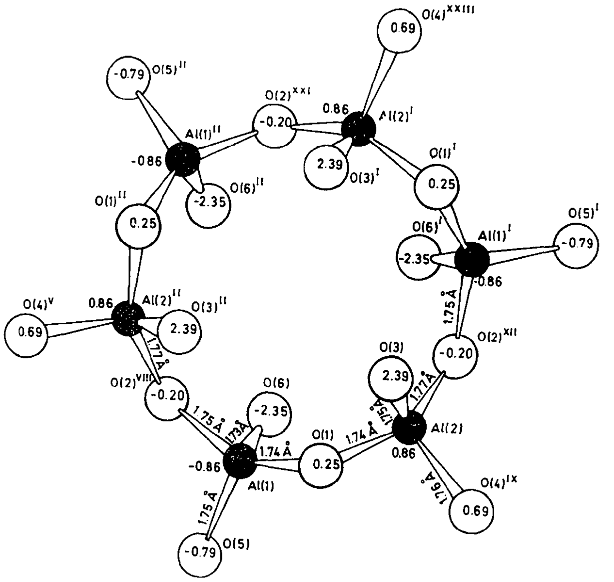


Fig. 4. An Al_6O_{18} puckered ring at $\frac{1}{8}\frac{1}{8}\frac{1}{8}$ viewed along $[\bar{1}\bar{1}\bar{1}]$. Heights from the mean Al plane are labelled in Å.

Crystal data

$Ca_3Al_2O_6$, $a=15{\cdot}263$ (3) Å (Cu $K\alpha$, $\lambda=1{\cdot}5405$ Å), $V=3556$ (2) Å^3, $D_m=3{\cdot}016$ (2) g cm^{-3}, $Z=24$, $D_x=3{\cdot}027$ (2) g cm^{-3}. Absorption coefficient for Cu $K\alpha$, $\mu=274{\cdot}6$ cm^{-1}. Crystal radius: 0·102 (3) mm. Laue symmetry: $m3$. Reflexions present: hkl, no conditions; $hk0$, $h=2n$; $0kl$, $k=2n$, $h0l$, $l=2n$. Space group: $Pa3$.

Structure determination

The three-dimensional Patterson synthesis showed only 128 definite peaks in the whole cell unit, but there are 72 Ca atoms, 48 Al atoms and 144 O atoms in the unit cell (giving over 14000 peaks from the Ca and Al atoms alone). Hence each of the heavy Patterson peaks consists of a large number of superimposed vector peaks, probably mainly Ca–Ca, Ca–Al and Al–Al. From the Patterson map and the pseudo-cell, it was concluded that the following positions in $Pa3$

Table 1. *Atomic positional parameters and anisotropic vibration components* ($\times 10^4$), *with e.s.d.'s in parentheses*

	x	y	z
Ca(1)	0·0000 (0)	0·0000 (0)	0·0000 (0)
Ca(2)	0·5000 (0)	0·0000 (0)	0·0000 (0)
Ca(3)	0·2561 (1)	0·2561 (1)	0·2561 (1)
Ca(4)	0·3750 (1)	0·3750 (1)	0·3750 (1)
Ca(5)	0·1386 (1)	0·3763 (1)	0·1272 (1)
Ca(6)	0·3800 (1)	0·3838 (1)	0·1209 (1)
Al(1)	0·2526 (1)	0·0133 (1)	0·0197 (1)
Al(2)	0·2444 (1)	0·2335 (1)	0·0046 (1)
O(1)	0·2777 (2)	0·1241 (2)	0·0103 (2)
O(2)	0·4835 (2)	0·1315 (2)	0·2536 (2)
O(3)	0·2664 (2)	0·2841 (2)	0·1049 (2)
O(4)	0·2350 (2)	0·4047 (2)	0·2921 (2)
O(5)	0·3491 (2)	−0·0385 (2)	−0·0174 (2)
O(6)	0·1509 (2)	−0·0104 (2)	−0·0242 (2)

Table 1 (*cont.*)

	U_{11}	U_{22}	U_{33}	$2U_{32}$	$2U_{31}$	$2U_{21}$
Ca(1)	60 (5)	60 (5)	60 (5)	28 (8)	28 (8)	28 (8)
Ca(2)	84 (5)	84 (5)	84 (5)	1 (8)	1 (8)	1 (8)
Ca(3)	79 (4)	79 (4)	79 (4)	13 (6)	13 (6)	13 (6)
Ca(4)	117 (5)	117 (5)	117 (5)	27 (6)	27 (6)	27 (6)
Ca(5)	79 (5)	90 (5)	223 (6)	−10 (6)	51 (7)	26 (6)
Ca(6)	60 (5)	92 (5)	96 (5)	11 (6)	23 (5)	−11 (6)
Al(1)	56 (6)	58 (6)	80 (7)	−11 (10)	−3 (9)	−22 (8)
Al(2)	78 (7)	59 (6)	65 (6)	9 (8)	15 (8)	−11 (9)
O(1)	170 (16)	97 (16)	176 (16)	−39 (20)	−25 (24)	−2 (23)
O(2)	138 (15)	86 (15)	188 (16)	−13 (22)	14 (22)	−39 (22)
O(3)	83 (13)	182 (15)	98 (13)	−61 (22)	67 (20)	−38 (21)
O(4)	142 (14)	94 (14)	191 (15)	54 (23)	77 (22)	−11 (20)
O(5)	90 (14)	159 (15)	147 (14)	−81 (23)	−62 (21)	44 (23)
O(6)	66 (14)	154 (14)	142 (14)	10 (22)	47 (22)	62 (20)

Table 2. *Vibration ellipsoid parameters*

	R.m.s. Displacement (Å)	Direction cosines with respect to *a,b,c* *l*	*m*	*n*
Ca(1)	0·0926	0·5774	0·5774	0·5774
	0·0655	−0·8165	0·4082	0·4082
	0·0655	0·0000	−0·7071	0·7071
Ca(2)	0·0922	0·8165	−0·4082	−0·4082
	0·0915	−0·5774	−0·5774	−0·5774
	0·0922	0·0000	0·7071	−0·7071
Ca(3)	0·0950	0·5774	0·5774	0·5774
	0·0851	−0·8165	0·4082	0·4082
	0·0851	0·0000	−0·7071	0·7071
Ca(4)	0·1181	0·5774	0·5774	0·5774
	0·1004	−0·8165	0·4082	0·4082
	0·1004	0·0000	−0·7071	0·7071
Ca(5)	0·0810	0·8210	−0·5465	−0·1650
	0·0994	0·5442	0·8361	−0·0693
	0·1517	0·1756	−0·0332	0·9839
Ca(6)	0·0735	0·9366	0·2055	−0·2839
	0·0971	0·2868	−0·8977	0·3344
	0·1004	0·1955	0·4023	0·8944
Al(1)	0·0662	0·7155	0·6787	0·1654
	0·0807	0·6748	−0·7330	0·0858
	0·0894	0·1765	0·0558	−0·9827
Al(2)	0·0712	0·2766	0·7394	−0·6138
	0·0832	0·0578	−0·6470	−0·7603
	0·0917	0·9601	−0·2252	0·1661
O(1)	0·0975	0·1875	0·9402	0·2842
	0·1210	0·9310	−0·2611	0·2550
	0·1393	0·3127	0·2175	−0·9246
O(2)	0·0860	0·3870	0·9215	0·0319
	0·1232	0·9216	−0·3875	0·0228
	0·1383	0·0322	0·0171	−0·9993
O(3)	0·0768	0·6887	−0·1517	−0·7090
	0·1000	0·6934	0·4248	0·5820
	0·1411	0·2127	−0·8926	0·3975
O(4)	0·0878	0·2629	0·9051	−0·3343
	0·1147	0·8343	−0·3871	−0·3926
	0·1500	0·4844	0·1766	0·8568
O(5)	0·0922	0·9519	−0·0448	0·3032
	0·1064	0·1749	−0·7441	−0·6447
	0·1428	0·2542	0·6676	−0·6997
O(6)	0·0658	0·9047	−0·3126	−0·2894
	0·1206	0·2295	−0·1864	0·9553
	0·1267	0·3570	0·9294	0·0941

were most probable for Ca and Al:

(*a*)	000	(4)			
(*b*)	$\frac{1}{2}$00	(4)			
(*c*)	(i) $\frac{3}{8}\frac{3}{8}\frac{3}{8}$;	(ii) $\frac{1}{4}\frac{1}{4}\frac{1}{4}$;	(iii) $\frac{1}{8}\frac{1}{8}\frac{1}{8}$		(8)
(*d*)	(i) $\frac{3}{8}\frac{3}{8}\frac{1}{8}$;	(ii) $\frac{3}{8}\frac{1}{8}\frac{1}{8}$;	(iii) $\frac{1}{4}\frac{1}{4}$0;	(iv) $\frac{1}{4}$00	(24)

Using the above positions, (*a*) 1×4, (*b*) 1×4, (*c*) 3×8, (*d*) 4×24, Ca and Al atoms can be placed in 24 different ways. 72 Ca atoms can be divided up between general and special positions as follows: 3×24; $2\times24+3\times8$; $2\times24+2\times8+2\times4$. 48 Al atoms can be accommodated similarly as: 2×24; $1\times24+3\times8$; $1\times24+2\times8+2\times4$. The compatible combinations are therefore:

(1)	Ca 3×24	Al $1\times24+3\times8$	(4)
(2)	Ca 3×24	Al $1\times24+2\times8+2\times4$	(12)
(3)	Ca $2\times24+3\times8$	Al 2×24	(6)
(4)	Ca $2\times24+2\times8+2\times4$	Al 2×24	(18)

The number in parentheses gives the possible permutations of positions in each combination. However, a number of these are equivalent if the origin is shifted from 000 to $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and hence the number of different arrangements is reduced from 40 to 24 unique ways.

Fourier syntheses, phased on the various possible heavy-atom arrangements obtained in this way, were calculated, and in those cases where possible oxygen positions were indicated, least-squares refinement was carried out. Until the twelfth trial the discrepancy index *R* did not drop below 45%. The structure which finally refined to $R=5\cdot1$% was obtained from the following heavy-atom positions belonging to group (4) combination, Ca 000, $\frac{1}{2}$00, $\frac{3}{8}\frac{3}{8}\frac{3}{8}$, $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, $\frac{3}{8}\frac{3}{8}\frac{1}{8}$, $\frac{3}{8}\frac{1}{8}\frac{1}{8}$; Al $\frac{1}{4}\frac{1}{4}$0, $\frac{1}{4}$00. The real cell of C_3A consists of 64 pseudo-cells ($a'=a/4$). The Ca atoms occupy 56 body-centring positions of the pseudo-cells leaving eight of them vacant, namely ($\frac{1}{8}\frac{1}{8}\frac{1}{8}$) and its symmetry-related positions. The 48 Al atoms and the remaining 16 Ca atoms occupy the corners of the pseudo-cells.

The Fourier map phased with these heavy atoms showed the approximate positions of the six oxygen atoms of the asymmetric unit. Three cycles of isotropic refinement converged to an *R* value of 8·6%. A further four cycles of anisotropic refinement were carried out with the measured weights for individual reflexions. The discrepancy index *R* was reduced to 5·1% and the shifts in atomic parameters were zero up to the fourth decimal place. The full-matrix *SFLS* program described by Cruickshank (1970) was used. The refined atomic parameters are given in Table 1. The vibrational ellipsoid axes (r.m.s. displacement) are given in Table 2. A composite Fourier map calculated at the end of the refinement is shown in Fig. 2.*

Description of structure

The unit cell of C_3A contains 72 Ca, 48 Al and 144 O atoms and in the asymmetric unit there are six Ca, two Al and six O atoms. Roman numeral notations for symmetry-related atom positions and the interatomic distances and angles are given in Tables 3 and 4. One-eighth of the unit cell (up to $x,y,z=\frac{1}{2}$) of the C_3A structure viewed along [0$\bar{1}$0] is shown in Fig. 3. The structure is built of sixfold rings centred on threefold axes and composed of two types of distorted AlO_4 tetrahedra. The holes in between the rings contain the Ca atoms. In the unit cell there are 80 such possible holes; 72 of them are filled up with Ca atoms leaving eight vacant on threefold axes at $\frac{1}{8}\frac{1}{8}\frac{1}{8}$ together with its symmetry-related positions.

The average Al–O bond length is 1·750 Å (range 0·039) for Al(1) and 1·754 Å (range 0·016) for Al(2).

* A list of structure factors is given by Mondal (1973) and has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30726 (9 pp.). Copies may be obtained through The Executive Secretary, International Union Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Notation for symmetry-related atom positions*

Atom superscripts	General equivalent positions	Atom superscripts	General equivalent positions
None	x,y,z	xii	$y,\frac{1}{2}-z,\frac{1}{2}+x$
i	z,x,y	xiii	$\frac{1}{2}+x,\frac{1}{2}-y,-z$
ii	y,z,x	xiv	$-x,\frac{1}{2}+y,\frac{1}{2}-z$
iii	$\frac{1}{2}+z,\frac{1}{2}-x,-y$	xv	$\frac{1}{2}-x,-y,\frac{1}{2}+z$
iv	$-y,\frac{1}{2}+z,\frac{1}{2}-x$	xvi	$-z,\frac{1}{2}+x,\frac{1}{2}-y$
v	$\frac{1}{2}-x,\frac{1}{2}+y,z$	xvii	$\frac{1}{2}-z,-x,\frac{1}{2}+y$
vi	$x,\frac{1}{2}-y,\frac{1}{2}+z$	xviii	$\frac{1}{2}+y,\frac{1}{2}-z,-x$
vii	$-z,-x,-y$	xix	$\frac{1}{2}-y,-z,\frac{1}{2}+x$
viii	$\frac{1}{2}-z,\frac{1}{2}+x,y$	xx	$-x,-y,-z$
ix	$z,\frac{1}{2}-x,\frac{1}{2}+y$	xxi	$\frac{1}{2}+x,y,\frac{1}{2}-z$
x	$\frac{1}{2}+z,x,\frac{1}{2}-y$	xxii	$-y,-z,-x$
xi	$\frac{1}{2}-y,\frac{1}{2}+z,x$	xxiii	$\frac{1}{2}+y,z,\frac{1}{2}-x$

The six AlO_4 tetrahedra in the Al_3O_{18} ring are tilted alternately to each side of the ring, so that each presents a face with two bridging oxygen atoms towards the vacant site. The six bridging oxygen atoms are almost coplanar, with the aluminum atoms alternately 0·8 Å up and down from the plane. The six oxygen atoms at the remaining corners of the inner faces lie 2·4 Å away from the plane of the ring and nearer to the threefold axis, three on each side of the ring. The six outer oxygens are alternately 0·7 Å up and down from the plane of the ring.

There are eight such separate Al_6O_{18} rings surrounding each of the eight vacant sites which are situated near the corners of eight sub-cells ($a''=a/2$). These eight rings account for all 48 Al and 144 O atoms in the unit cell. A diagram of the Al_6O_{18} puckered ring surrounding the hole at $\frac{1}{8}\frac{1}{8}\frac{1}{8}$, viewed along $[\bar{1}\bar{1}\bar{1}]$ is shown in Fig. 4. The effective radius of the approximately spherical hole, with centre point very near to $\frac{1}{8}\frac{1}{8}\frac{1}{8}$, is 1·47 Å, assuming an ionic radius of 1·40 Å for the surrounding O atoms.

There are six types of Ca atoms in the structure. Ca(1) at the origin with symmetry $\bar{3}$, is coordinated at a distance of 2·34 Å to six oxygen atoms of one type O(6), forming an octahedron which is compressed along the threefold axis. The O–Ca–O angles are 77·77° and 102·23° and the distance between the two planes of O atoms normal to the threefold axis is shorter by 0·64 Å than that for a regular octahedron. $Ca(2)^{xiv}$ at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, symmetry $\bar{3}$, is also octahedrally coordinated at 2·39 Å to oxygen atoms of one type O(5), with O–Ca–O angles 80·99° and 99·01°. The $Ca(2)^{xiv}$ octahedron is slightly less compressed than that of Ca(1). The Ca(3) atom on the threefold axis is surrounded by six oxygen atoms generated from two types of oxygen positions, O(3) and O(4) at approximately 2·35 Å, by the operation of threefold symmetry. The oxygen atoms form a distorted trigonal prism. Ca(4), also lying on the threefold axis, is surrounded by six oxygen atoms generated from O(1) and O(4) at approximately 2·53 Å and three more at 3·01 Å generated from O(5). The atom Ca(5) in a general position is irregularly coordinated to eight oxygen atoms, five with Ca–O distances from 2·26 to 2·57 Å and three with 2·95 to 2·97 Å. Five types of oxygen atoms are involved in bonding to Ca(5). One oxygen atom is derived from each of O(1) and O(4) and two each from O(2), O(3) and O(5). $O(5)^{i}$ at a distance of 3·5 Å might be taken into consideration for very weak electrostatic bonding to Ca(5). In the neighbourhood of Ca(6) six oxygen atoms, with Ca–O distances from 2·27 to 2·78 Å, are generated from four types, *i.e.* one each from O(2), O(3) and O(4) and three from O(6). These six oxygen atoms are not evenly distributed around Ca(6) and leave an opening through which there may be some weak electrostatic bonding with $O(1)^{xi}$ and O(4) at 3·1 and 3·4 Å. The Ca–O bonds for Ca(4), Ca(5), Ca(6) are shown in stereograms (Fig. 5*a*,*b*,*c*).

Table 4. *Distances and angles with e.s.d.'s in parentheses*

	Number of equivalents	Length (Å)		Number of Equivalents	Angle (°)
Ca(1)–O(6)	6	2·338 (3)	$O(6)$—Ca(1)–$O(6)^{i}$	6	102·23 (9)
			$O(6)$—Ca(1)–$O(6)^{vii}$	6	77·77 (9)
Ca(2)–O(5)	6	2·391 (3)	$O(5)$—Ca(2)–$O(5)^{iii}$	6	99·01 (10)
			$O(5)$—Ca(2)–$O(5)^{viii}$	6	80·99 (10)
Ca(3)–O(3)	3	2·351 (3)	$O(3)$—Ca(3)–$O(3)^{i}$	3	103·42 (10)
Ca(3)–O(4)	3	2·357 (3)	O(3)—Ca(3)–O(4)	3	93·60 (10)
			$O(3)$—Ca(3)–$O(4)^{i}$	3	162·50 (11)
			$O(4)$—Ca(3)–$O(4)^{i}$	3	86·49 (12)
			$O(3)$—Ca(3)–$O(4)^{ii}$	3	76·05 (10)
$Ca(4)–O(1)^{vi}$	3	2·543 (3)	$O(1)^{vi}$–Ca(4)–$O(1)^{x}$	3	118·23 (4)
Ca(4)–O(4)	3	2·525 (3)	$O(1)^{vi}$–Ca(4)–O(4)	3	84·92 (10)
$Ca(4)–O(5)^{vi}$	3	3·012 (3)	$O(1)^{vi}$–Ca(4)–$O(4)^{i}$	3	64·27 (10)
			$O(1)^{vi}$–Ca(4)–$O(4)^{ii}$	3	142·59 (11)
			$O(1)^{vi}$–Ca(4)–$O(5)^{vi}$	3	58·48 (9)
			$O(1)^{xi}$–Ca(4)–$O(5)^{vi}$	3	69·36 (10)
			$O(1)^{x}$–Ca(4)–$O(5)^{vi}$	3	126·02 (11)
			$O(4)$—Ca(4)–$O(4)^{i}$	3	79·43 (12)
			$O(4)$—Ca(4)–$O(5)^{vi}$	3	90·81 (10)
			$O(4)^{ii}$–Ca(4)–$O(5)^{vi}$	3	154·17 (9)
			$O(4)^{i}$–Ca(4)–$O(5)^{vi}$	3	122·53 (9)
			$O(5)^{vi}$–Ca(4)–$O(5)^{x}$	3	74·27 (10)

Table 4 (*cont.*)

	Length (Å)		Angle (°)
Ca(5)–O(1)^{i}	2·471 (3)	O(1)^{i}—Ca(5)–O(2)^{i}	174·52 (11)
Ca(5)–O(2)^{i}	2·401 (3)	O(1)^{i}—Ca(5)–O(2)^{xii}	63·16 (9)
Ca(5)–O(2)^{xii}	2·958 (3)	O(1)^{i}—Ca(5)–O(3)	106·33 (11)
Ca(5)–O(3)	2·429 (3)	O(1)^{i}—Ca(5)–O(3)^{i}	62·22 (9)
Ca(5)–O(3)^{i}	2·969 (3)	O(1)^{i}—Ca(5)–O(4)	120·10 (9)
Ca(5)–O(4)	2·947 (3)	O(1)^{i}—Ca(5)–O(5)^{v}	110·49 (11)
Ca(5)–O(5)^{v}	2·569 (3)	O(1)^{i}—Ca(5)–O(5)^{iv}	84·49 (12)
Ca(5)–O(5)^{iv}	2·258 (3)	O(2)^{i}—Ca(5)–O(2)^{xii}	120·26 (7)
		O(2)^{i}—Ca(5)–O(3)	79·14 (11)
		O(2)^{i}—Ca(5)–O(3)^{i}	119·33 (11)
		O(2)^{i}—Ca(5)–O(4)	60·76 (10)
		O(2)^{i}—Ca(5)–O(5)^{v}	67·97 (11)
		O(2)^{i}—Ca(5)–O(5)^{iv}	90·05 (12)
		O(2)^{xii}–Ca(5)–O(3)	62·46 (10)
		O(2)^{xii}–Ca(5)–O(3)^{i}	102·30 (9)
		O(2)^{xii}–Ca(5)–O(4)	138·60 (9)
		O(2)^{xii}–Ca(5)–O(5)^{v}	72·87 (9)
		O(2)^{xii}–Ca(5)–O(5)^{iv}	125·11 (11)
		O(3)—Ca(5)–O(3)^{i}	85·68 (13)
		O(3)—Ca(5)–O(4)	78·70 (9)
		O(3)—Ca(5)–O(5)^{v}	96·59 (11)
		O(3)—Ca(5)–O(5)^{iv}	169·31 (12)
		O(3)^{i}—Ca(5)–O(4)	58·71 (8)
		O(3)^{i}—Ca(5)–O(5)^{v}	172·69 (10)
		O(3)^{i}—Ca(5)–O(5)^{iv}	99·19 (10)
		O(4)—Ca(5)–O(5)^{v}	128·52 (10)
		O(4)—Ca(5)–O(5)^{iv}	95·48 (11)
		O(5)^{v}—Ca(5)–O(5)^{iv}	79·79 (13)
Ca(6)–O(1)^{xi}	3·075 (3)	O(1)^{xi}—Ca(6)–O(2)^{i}	62·96 (9)
Ca(6)–O(2)^{i}	2·462 (3)	O(1)^{xi}—Ca(6)–O(3)	118·54 (10)
Ca(6)–O(3)	2·320 (3)	O(1)^{xi}—Ca(6)–O(4)^{ii}	78·06 (11)
Ca(6)–O(4)^{ii}	2·266 (3)	O(1)^{xi}—Ca(6)–O(6)^{v}	104·58 (10)
Ca(6)–O(6)^{v}	2·781 (3)	O(1)^{xi}—Ca(6)–O(6)^{iii}	136·92 (11)
Ca(6)–O(6)^{iii}	2·294 (3)	O(1)^{xi}—Ca(6)–O(6)^{xi}	61·17 (10)
Ca(6)–O(6)^{xi}	2·477 (3)	O(2)^{i}—Ca(6)–O(3)	80·03 (11)
		O(2)^{i}—Ca(6)–O(4)^{ii}	117·49 (11)
		O(2)^{i}—Ca(6)–O(6)^{v}	63·94 (10)
		O(2)^{i}—Ca(6)–O(6)^{iii}	133·65 (12)
		O(2)^{i}—Ca(6)–O(6)^{xi}	105·48 (11)
		O(3)—Ca(6)–O(4)^{ii}	78·44 (12)
		O(3)—Ca(6)–O(6)^{v}	99·83 (11)
		O(3)—Ca(6)–O(6)^{iii}	104·33 (11)
		O(3)—Ca(6)–O(6)^{xi}	172·40 (11)
		O(4)^{ii}—Ca(6)–O(6)^{v}	177·33 (11)
		O(4)^{ii}—Ca(6)–O(6)^{iii}	108·44 (11)
		O(4)^{ii}—Ca(6)–O(6)^{xi}	94·26 (11)
		O(6)^{v}—Ca(6)–O(6)^{iii}	69·92 (12)
		O(6)^{v}—Ca(6)–O(6)^{xi}	87·40 (13)
		O(6)^{iii} –Ca(6)–O(6)^{xi}	75·83 (13)
Al(1)—O(1)	1·741 (3)	O(1)—Al(1)–O(2)^{viii}	109·97 (18)
Al(1)—O(2)^{viii}	1·768 (4)	O(1)—Al(1)–O(5)	102·96 (16)
Al(1)—O(5)	1·766 (3)	O(1)—Al(1)–O(6)	111·62 (16)
Al(1)—O(6)	1·729 (3)	O(2)^{viii}–Al(1)–O(5)	103·85 (16)
		O(2)^{viii}–Al(1)–O(6)	105·83 (15)
		O(5)—Al(1)–O(6)	122·11 (17)
Al(2)—O(1)	1·749 (3)	O(1)—Al(2)–O(2)^{xii}	113·58 (17)
Al(2)—O(2)^{xii}	1·764 (3)	O(1)—Al(2)–O(3)	108·86 (17)
Al(2)—O(3)	1·748 (3)	O(1)—Al(2)–O(4)^{ix}	100·61 (16)
Al(2)—O(4)^{ix}	1·757 (3)	O(2)^{xii}–Al(2)–O(3)	107·36 (16)
		O(2)^{xii}–Al(2)–O(4)^{ix}	102·46 (16)
		O(3)—Al(2)–O(4)^{ix}	124·01 (16)

O(1)—O(2)^{viii}	2·874 (4)	O(1)—O(2)^{xii}	2·937 (4)
O(1)—O(5)	2·743 (4)	O(1)—O(3)	2·842 (4)
O(1)—O(6)	2·870 (4)	O(1)—O(4)^{ix}	2·696 (4)
O(5)—O(2)^{viii}	2·782 (4)	O(3)—O(2)^{xii}	2·830 (4)
O(6)—O(2)^{viii}	2·789 (4)	O(2)^{xii}–O(4)^{ix}	2·745 (4)
O(5)—O(6)	3·058 (4)	O(3)—O(4)^{ix}	3·095 (4)

Discussion

(*a*) *Reactivity*

C_3A is highly reactive with water. Immediately after contact with water the hydration product of C_3A is $2CaO.Al_2O_3.8H_2O$ (C_2AH_8) and at 20°C and above it is gradually converted to hexahydrate (C_3AH_6). The structure of C_3A contains eight discrete holes of approximate radius 1·47 Å and both Ca(1) and Ca(2)^{xiv} octahedra are compressed along the three-fold axis. The other Ca coordinations to O atoms are

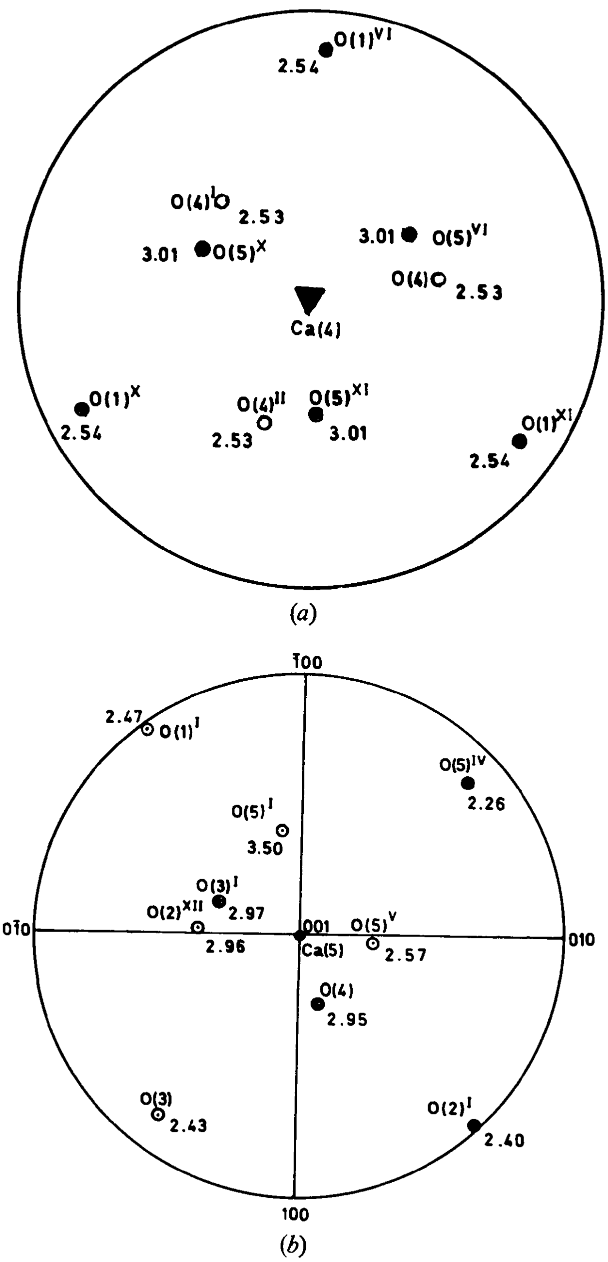
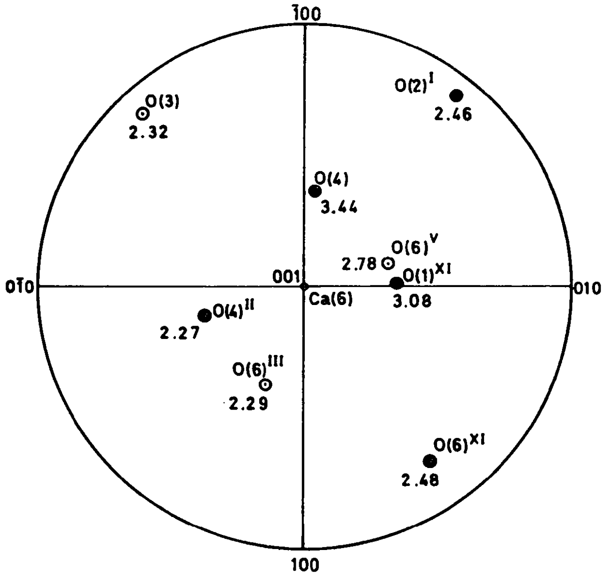


Fig. 5. Ca–O bonds shown on stereograms. Bond lengths are labelled in Å. (*a*) Ca(4)–O; (*b*) Ca(5)–O.

rather irregular. The observed minimum Ca–O distances 2·26 and 2·27 Å around Ca(5) and Ca(6) are short in comparison with observed Ca–O bond distances in other cement compounds such as $3CaO.SiO_2$ (Jeffery, 1952), $CaO.2Al_2O_3$ (Ponomarev, Kheiker & Belov, 1971) where the minimum Ca–O bond distances were found to be 2·29 Å. The distortion in the octahedral arrangement of oxygen atoms and the presence of short Ca–O bonds indicates a certain amount of strain



(*c*)

Fig. 5 (*cont.*) (*c*) Ca(6)–O.

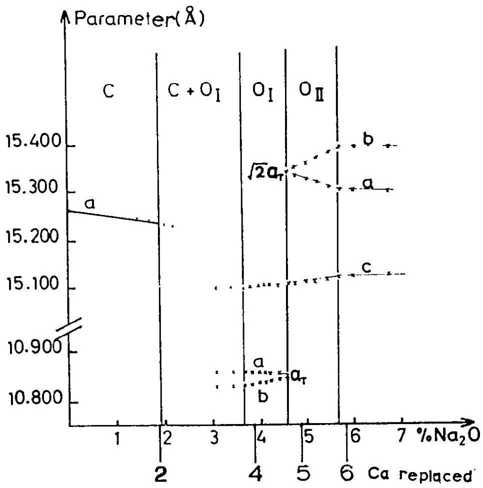


Fig. 6. Diagram showing the variation of cell parameters of solid solutions of $Ca_3Al_2O_6 + Na_2O$ as a function of the percentage of Na_2O and also the replacement of Ca atoms by Na atoms, each Ca being replaced by two Na (after Regourd, Chromy, Hjorth, Mortureux & Guinier, 1973).

and hence there will be potential energy stored up in the structure. This potential energy will be available to assist the break up of the structure under the action of water and the production of hydroxyl, hydroxylated aluminate and calcium ions in solution which then combine to crystallize out as C_2AH_8. The presence of the hole in the structure may facilitate the action of water in this process.

(*b*) *Solid solution series*

C_3A forms solid solutions with some minor components such as Na_2O, MgO, K_2O, Fe_2O_3 *etc.*, present in Portland cement. An extensive study on Na_2O–$Ca_3Al_2O_6$ solid solution series using X-ray powder and other physical methods has been made by Regourd, Chromy, Hjorth, Mortureux & Guinier (1973). On the X-ray pattern they observed close splitting of the cubic 440, 008 and 844 lines and deduced the existence of three crystalline forms, cubic, orthorhombic I, *O*(I) and orthorhombic II, *O*(II), and the results are shown in Fig. 6. At higher temperatures, above 500°C, they observed the transition of *O*(I) and *O*(II) phases to a tetragonal phase. The transition from *O*(I) to tetragonal is continuous, whereas *O*(II) to tetragonal is discontinuous.

A simple replacement of one mol CaO by one mol Na_2O is equivalent to replacing one Ca^{2+} by two Na^+. Eight holes occur on threefold axes in each unit cell of the structure of C_3A into which extra atoms could fit. Since the sizes of Ca^{2+} and Na^+ are comparable it is almost certain that Na^+ ions go in the holes of the structure. If one Na^+ ion occupies a vacant site such as $\frac{1}{8}\frac{1}{8}\frac{1}{8}$, another Na^+ ion will replace a Ca^{2+} ion as near as possible to the vacant site in order to achieve a localized balancing of charges. The two Ca atoms, Ca(1) at 000 and Ca(3) at $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, are the nearest to the proposed Na^+ at $\frac{1}{8}\frac{1}{8}\frac{1}{8}$. The Na–Ca(1) and Na–Ca(3) distances are 3·30 and 3·46 Å. These two Ca atoms have different relations to the holes in the structure; Ca(1) has another hole next to it at $-\frac{1}{8}-\frac{1}{8}-\frac{1}{8}$, whereas Ca(3) has no other adjacent hole. It is by no means obvious which substitution would be energetically more favourable, and a structure determination of the substituted C_3A is required to determine the Na positions and the rearrangement of the bonding.

Since the sizes of Ca^{2+} and Na^+ are comparable, and the radius of the hole in C_3A is greater than that of Na^+, the effect of solid solution should be to attract the O^{2-} ions round the hole towards Na^+ at $\frac{1}{8}\frac{1}{8}\frac{1}{8}$ and reduce the total volume of the cell, leading to the observed decrease in *a*. The cubic symmetry of individual unit cells must be destroyed, since no cubic space group has two or four equivalent positions on a threefold axis, but if the substitution occurs randomly in different unit cells, overall cubic symmetry may be preserved as a statistical effect in the crystal as a whole and its diffraction pattern. Up to the filling of two holes by Na^+, *i.e.*, the replacement of $2Ca^+$ by

$4Na^+$ in the unit cell or 1·9% solid solution of Na_2O, this statistical effect occurs. At 3·7% Na_2O, when almost four out of eight holes are filled, the general arrangement is altered to produce the centring of the base of the cubic cell and its distortion into a rhombus whose diagonals give an orthorhombic cell of half the volume of the cubic cell. Between the filling of 2 and 4 holes (1·9–3·7% Na_2O) a mixture of C and O(1) occurs.

The solid solution of 4·6% Na_2O in C_3A corresponds nearly to the replacement of $5Ca^{2+}$ by $10Na^+$. In the range of 3·7–4·6% Na_2O, the same orthorhombic form (I) occurs. This presumably means that the replacement of more than four up to five Ca occurs randomly (possibly over a limited number of sites) thus preserving an orthorhombic cell as a statistical effect. Between 4·6 and 5·7% Na_2O a new form occurs with a structural and cell parameter discontinuity at 4·6%. At 5·7% Na_2O six out of eight holes are occupied by Na^+, and this form might be expected to return to an approximation to the original cubic structure, with two holes unfilled, instead of two holes filled, but in fact this appears to be the limit of binary solid solution.

There is some conflict of evidence on the high Na_2O form. Regourd *et al.* (1973) deduce from excellent X-ray evidence that this form is orthorhombic [*O*(II)] with cell parameters similar to those of the original cubic form, and face centring no longer occurring. Maki (1973), finds monoclinic symmetry mainly from optical evidence and a smaller unit cell, which would imply *C*-centring in *O*(II). At higher temperatures (above 400°C) both *O*(I) and the high Na_2O form transform to tetragonal, and this structure can be quenched to metastable existence at room temperature. The tetragonal structure is similar to orthorhombic I, into which it transforms continuously and may have full tetragonal symmetry (*i.e.*, not statistical symmetry) for a replacement of 4 Ca by 8 Na in the large pseudo-cubic cell, which means 2 Ca by 4 Na in the primitive tetragonal cell.

It would be expected that the high reactivity of C_3A with water would decrease due to the filling of most of the holes in the solid solution of Na_2O–$Ca_3Al_2O_6$. The rate of hydration for a laboratory preparation approaching $Na_2O.8CaO.3Al_2O_3$ was, in fact, found to be much less than that of C_3A (Murakami, Tanaka & Nakura, 1968). However, there is some evidence that this is not the case in actual cements (Forrester & Skalny, 1968). Two commercial cements were selected to be as similar as possible, but one containing cubic C_3A and the other a dark prismatic form, containing both K and Na. These were examined by conduction calorimetry and that which contained the non-cubic C_3A showed much earlier and larger heat generation. There are possible explanations for this, other than crystallographic. The surface area of the prismatic form may have been greater or the presence of K in the prismatic phase may alter the solubility.

(c) Relation to other structures

Maki & Sugimura (1970) showed that C_3A and N_2CS_3 have the same space group and similar cell sizes and powder diffraction patterns. The unit cells each contain 144 O atoms and 48 Al or Si atoms. C_3A has 72 Ca atoms, N_2CS_3 has 64 Na and 16 Ca atoms, *i.e.*, eight additional cations. Maki & Sugimura suggested that 'the structure of C_3A may contain suitable spaces to include the eight additional cations'. This is indeed the case, and if N_2CS_3 is fully ordered the 16 Ca atoms must be at 000; $00\frac{1}{2}$ (4) and one of $\frac{1}{8}\frac{1}{8}\frac{1}{8}$; $\frac{1}{4}\frac{1}{4}\frac{1}{4}$; $\frac{3}{8}\frac{3}{8}\frac{3}{8}$ (8) or in two of the eightfold positions. The most probable positions for the 16 Ca atoms are 000, $00\frac{1}{2}$, $\frac{1}{4}\frac{1}{4}\frac{1}{4}$, giving a Ca on either side of the Si_6O_{18} rings, with Na atoms occupying all the body centring positions of the pseudo-cells ($a'=a/4$), including the holes of the C_3A structure. However, only a refinement of the various possible structures, using accurate intensity data, can determine which is correct.

Whatever the arrangement of the Na and Ca atoms, it seems fairly certain that a six-membered Si_6O_{18} ring exists in this compound.

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The Structure of an Ascorbate Precursor: 2-Keto-L-gulonic Acid Monohydrate

By J. Hvoslef and B. Bergen

Department of Chemistry, University of Oslo, Blindern, Oslo 3, *Norway*

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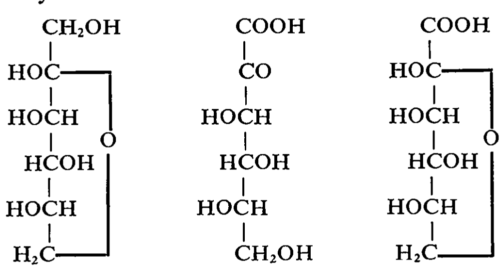
The crystal structure of 2-keto-L-gulonic acid monohydrate $C_6H_{10}O_7.H_2O$ has been determined by X-ray diffraction with an automatic diffractometer and Mo $K\alpha$ radiation. The space group is $P2_12_12_1$ with $a=16{\cdot}469$ (2), $b=7{\cdot}853$ (1), $c=6{\cdot}808$ (1) Å. The parameters were refined to $R=0{\cdot}044$ and R(weighted) = 0·028 for 1393 reflexions. The average standard deviations are 0·0026 Å and 0·2° for non-hydrogen atoms. The molecular and crystal structure resembles that of α-sorbose, although the hydrogen-bond system is different. The α-anomeric C(2)–O(2)H bond length is 1·381 Å, and the combined effect of this and the adjacent COOH group gives rise to a difference of 0·022 Å in the C–O bonds of the pyranoid ring. The carboxyl group is almost coplanar with the anomeric hydroxyl substituent. All the oxygen atoms participate in hydrogen bonding, and the water molecule connects four different sugar molecules, both within and between the helical chains. The relationships to the bonding properties of L-ascorbic acid are discussed.

Introduction

The production of L-ascorbic acid (vitamin C) starting with D-glucose has L-sorbose (I) and 2-keto-L-gulonic acid (II/III) as the most important intermediates. The latter compound is readily converted to L-ascorbic acid by means of acids, but in alkaline media the process is rather slow and unwilling. Formulation of the structure as an open chain (II) comprising a free carbonyl group has been questioned by Reichstein (1936) who instead proposed a structure involving a pyranoid lactol ring (III) which would explain the stability towards alkali.



(I) (II) (III)

The conversion of 2-keto-L-gulonic acid to L-ascorbic acid proceeds according to Euler & Eistert (1957) by the opening of the pyranoid ring, formation of an oxonium cation, enolization and lactonization. A corresponding process is presumably also taking place *in vivo* during the formation of vitamin C. L-Ascorbic acid may thus be described as the γ-lactone of the enediolic form of (II).

Our investigation was undertaken to establish the molecular structure and conformation of this acid and to compare the results with the values found by Kim & Rosenstein (1967) for the α-anomer of L-sorbose, and also to study its relationship to L-ascorbic acid.

Experimental

Commercially available 2-keto-L-gulonic acid monohydrate, $C_6H_{10}O_7.H_2O$ (Merck), was recrystallized from water, giving a m.p. of 162°C. A transparent, colourless prismatic specimen with the dimensions 0·17 × 0·06 × 0·028 cm was used for the collection of X-ray data. The space group was identified as $P2_12_12_1$ from systematic absences on Weissenberg photographs. The crystal was mounted on an automatic Picker four-angle diffractometer with the c axis slightly inclined to the φ axis of the goniometer. The diffractometer was operated in the usual ω–2θ mode, with Mo $K\alpha$ radiation ($\lambda=0{\cdot}7107$ Å). By restricting $2\theta_{max}$ to 70°, 2159 reflexions were considered, but only 1393 were clearly above the background. The stability of