The Crystal Structure of Pentacalcium Trialuminate, 5CaO.3Al$_2$O$_3$*

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The metastable phase 5CaO.3Al$_2$O$_3$ (better known as 'unstable C$_5$A$_3$,' to cement chemists) crystallizes in the orthorhombic space group $Cmc2_1$ (not $C222_1$ as previously reported) with $a = 11 \cdot 253$, $b = 10 \cdot 966$, $c = 10 \cdot 290$ Å, $Z = 4$. The space group could be determined unambiguously from examination of a Patterson map in conjunction with stereochemical considerations. The structure was solved by an iterative process and refined to an R of 9·8% with eye-estimated film data. It consists of alternating twisted sheets of distorted AlO$_4$ tetrahedra and layers of Ca atoms which lie perpendicular to [001]. The tetrahedra are linked through corners to form a network of five-membered rings. The arrangement of the Ca atoms in a layer presents some unusual features in that some of the Ca–Ca distances are very short (3·200–3·267 Å) resulting in face-sharing of certain of the Ca polyhedra. Variations in cation–oxygen distances are discussed and a possible explanation for the short Ca–Ca contacts is put forward. As a consequence of its similarity to gehlenite, 2CaO.Al$_2$O$_3$.SiO$_2$, 5CaO.3Al$_2$O$_3$ provides no other basis from which the structures of the group of optically and crystallographically related compounds of interest to cement chemists may be determined.

Introduction

Shepherd, Rankin & Wright (1909) reported a stable and an unstable form of 5CaO.3Al$_2$O$_3$ with distinct optical characteristics. A structure determination and a consideration of crystal density of the stable form led Büssem & Eitel (1936) to suggest that its composition was 12CaO.7Al$_2$O$_3$ and not 5CaO.3Al$_2$O$_3$ as first supposed. This was later confirmed by Bartl & Scheller (1970).

Sundius (1939) found that a pleochroic mineral with similar optical properties to 'unstable 5CaO.3Al$_2$O$_3$' (as it was then called) existed in certain high-alumina cements. Parker (1954), as a result of phase-equilibrium studies, demonstrated that the pleochroic mineral was not unstable 5CaO.3Al$_2$O$_3$ as described by Shepherd *et al.* (1909), but a quaternary compound existing in the system CaO–Al$_2$O$_3$–FeO–SiO$_2$ (subsequently called 'pleochroite') with an MgO analogue (MgO replacing FeO).

Extensive investigations into the properties of these quaternary compounds have been made, the results of which have been summarized by Midgley (1968) in his paper on their probable compositions from X-ray microprobe analysis. In his report Midgley writes that J. H. Welch, during his investigations in the system CaO–Al$_2$O$_3$–MgO–SiO$_2$, discovered that 'unstable

5CaO.3Al$_2$O$_3$' was in fact a metastable phase of the same composition, the optical and some crystallographic properties of which have been described by Aruja (1957). It was also shown that this compound was not the pleochroic mineral found in high-alumina cement.

Majumdar (1964), continuing the work begun by Welch, demonstrated that the quaternary-phase Mg analogue of pleochroite, two new ternary compounds discovered by Welch during his investigations, gehlenite (2CaO.Al$_2$O$_3$.SiO$_2$) and 5CaO.3Al$_2$O$_3$ all had similar optical and crystallographic properties. [Aruja (1957), in fact, had already pointed out similarities in X-ray powder patterns and unit cells of gehlenite and 5CaO.3Al$_2$O$_3$ from which he drew conclusions about some possible relations between the two structures. Later Midgley (1962) reported that the quaternary Mg phase and pleochroite were crystallographically identical.] Although Majumdar (1964) found a common subcell from interpretations of powder photographs in all the compounds he investigated, he was unable to find any direct proof of its existence from X-ray single-crystal photographs, nor could a constant chemical content be derived for this subcell. He further deduced that apart from 5CaO.3Al$_2$O$_3$, none of the structures of these compounds could be based on the known structure of gehlenite.

Midgley (1968) determined compositions for the two quaternary phases and used the subcell property to derive possible structures for them. He also proposed possible structures for the ternary phases and 5CaO.3Al$_2$O$_3$, none of which was based on the gehlenite structure.

To summarize, it was shown that an insight into

the apparently complicated structures of the two ternary and two quaternary phases could not be gained by considering their structures as extensions of the known structure of gehlenite, in spite of their similar optical and crystallographic properties. Furthermore, the structure of $5CaO.3Al_2O_3$, which shows analogous properties to the others, was probably different from that of gehlenite. Consequently a structure determination of $5CaO.3Al_2O_3$ would have supplementary importance if the structures of these phases could be deduced from it.

Experimental

Attempts at growing single crystals of $5CaO.3Al_2O_3$ by the hot-stage-microscope technique from melts prepared following the method of Welch as described by Aruja (1957) were unsuccessful. Similar attempts with similar results were made at the Building Research Establishment, Watford, by the same technique from the original melt prepared by Welch (catalogued E60) from which he successfully grew single crystals of this phase for Aruja. In all cases it was not possible to isolate the single phase of $5CaO.3Al_2O_3$. However, the polycrystalline lumps, described by Welch as 'massive crystals' of $5CaO.3Al_2O_3$ and used by Aruja in density determinations, were located. Welch grew these from E60 in a furnace heated to 1450°C in a stream of nitrogen gas, the exact procedure being unknown.

From one of these lumps large single crystals could be isolated which were confirmed to be $5CaO.3Al_2O_3$ from subsequent examination by X-ray techniques. In order to reduce these crystals to a size suitable for data collection, attempts were made at grinding them into spheres and cylinders. These, however, were unproductive owing to the readiness of the crystals to cleave parallel to (001).

The density of the material was redetermined by flotation in a mixture of CCl_4 and CH_2I_2. The result $(3.06 \pm 0.01$ g cm$^{-3})$ was in good agreement with that of Aruja and corresponds to $Z = 4$.

It was apparent from the systematic absences of reflections in Weissenberg films that the assignment of the space group $C222_1$ was incorrect. In this investigation reflections hkl were found to be present only if $h + k$ was even, and $h0l$ only if l was even (Aruja's a and b axes interchanged), which correspond to space groups $Cmcm$, $Cmc2_1$ and $C2cm$.

Although a piezoelectric test proved inconclusive, the true space group was determined unambiguously as $Cmc2_1$ from examinations of Harker lines and sections in a Patterson map in conjunction with stereochemical considerations.

Intensities of reflections were collected by the equi-inclination Weissenberg method with Mo $K\alpha$ radiation from two small crystal flakes of roughly circular cross-section (due to grinding) mounted about two different crystallographic axes. The crystals had approximate radii of 0.19 and 0.1 mm, and thicknesses of 0.06 and 0.09 mm respectively. The spots were slightly integrated in the case of the smaller crystal in order to increase their size. Data, corresponding to the layers $0kl–10kl$ for the smaller crystal and $hk0–hk2$ for the larger, were recorded by the multiple-film technique on films of different speeds. The intensities were estimated visually against prepared scales and where necessary approximate spot-shape corrections were applied. 2172 and 428 reflections, corresponding to the two different settings, were measured of which 340 and 70, respectively, were classed as unobserved. These were given a value of half the minimum observable intensity. There was a certain amount of overlap between the two sets of data involving about 150 reflections.

Film correlation factors were determined with a program based on the method of Hamilton, Rollett & Sparks (1965) but no correlations between the two sets of data to produce interlayer scaling was attempted. (All the data, however, were used in the structure refinement.) The raw intensities were corrected for Lorentz and polarization effects but not for absorption.

The cell parameters, calculated from 2θ values of 41 high-angle reflections and refined by least squares, were $a = 11.253$ (6), $b = 10.966$ (6) and $c = 10.290$ (6) Å (e.s.d.'s in parentheses).

Structure determination

The structure was determined by an iterative process. Interpretations of a Patterson map provided the starting point for the solution as well as serving as a

Table 1. *Atomic coordinates* $(\times 10^4)$ *for* $5CaO.3Al_2O_3$ *with e.s.d.'s in parentheses*

	x	y	z
Ca(1)	1584 (2)	1075 (1)	2500*
Ca(2)	3578 (2)	3189 (1)	2000 (2)
Ca(3)	0	5240 (2)	2400 (3)
Al(1)	3573 (3)	1472 (2)	5093 (3)
Al(2)	0	2983 (3)	4393 (4)
Al(3)	0	−16 (3)	4630 (4)
Al(4)	2444 (3)	4012 (2)	4759 (3)
O(1)	2850 (6)	2757 (4)	5760 (5)
O(2)	0	6319 (8)	5690 (10)
O(3)	2754 (5)	235 (5)	5851 (6)
O(4)	3748 (6)	4376 (5)	3851 (6)
O(5)	0	1442 (6)	3873 (9)
O(6)	3410 (7)	1500 (5)	3405 (6)
O(7)	0	90 (8)	6320 (8)
O(8)	1287 (7)	3669 (6)	3707 (7)
O(9)	0	3013 (8)	6071 (8)

* z coordinate used to fix the origin.

means of checking atomic positions determined from subsequent Fourier syntheses. Four pairs of x and y coordinates, corresponding to the four possible choices of origin in the xy plane, were deduced from Harker sections for each of two Ca atoms. (The z coordinates are indeterminate in such a map owing

to the polar nature of $Cmc2_1$ in this direction.) On the assumption that the structure was of the layer type (in view of the strong cleavage plane perpendicular to [001]) and hence the z coordinates of the two Ca atoms equal, the problem of which pairs of coordinates belong to which origin could be overcome from a

Table 2. *Important interatomic distances and angles in* $5CaO.3Al_2O_3$

a	b	Distance ab (Å)	$a-b-c$	Angle abc (°)	a	b	Distance ab (Å)	$a-b-c$	Angle abc (°)
Ca(1)	O(1)	2·292 (5)	O(1)—Ca(1)—O(3)	69·9 (2)	Al(1)	O(1)	1·766 (5)	O(1)—Al(1)—O(2)	109·0 (3)
Ca(1)	O(3)	2·584 (7)	O(1)—Ca(1)—O(4)	161·4 (2)	Al(1)	O(2)	1·727 (5)	O(1)—Al(1)—O(3)	101·3 (3)
Ca(1)	O(4)	2·354 (6)	O(1)—Ca(1)—O(5)	126·5 (3)	Al(1)	O(3)	1·810 (7)	O(1)—Al(1)—O(6)	111·6 (4)
Ca(1)	O(5)	2·310 (6)	O(1)—Ca(1)—O(6)	87·5 (2)	Al(1)	O(6)	1·747 (6)	O(2)—Al(1)—O(3)	104·3 (4)
Ca(1)	O(6)	2·302 (7)	O(1)—Ca(1)—O(7)	96·0 (3)		Mean	1·763	O(2)—Al(1)—O(6)	117·0 (4)
Ca(1)	O(7)	2·507 (7)	O(3)—Ca(1)—O(4)	91·7 (2)				O(3)—Al(1)—O(6)	112·6 (3)
	Mean	2·367	O(3)—Ca(1)—O(5)	153·1 (2)					
			O(3)—Ca(1)—O(6)	85·6 (2)	O(1)	O(2)	2·889 (7)		
			O(3)—Ca(1)—O(7)	76·2 (2)	O(1)	O(3)	2·769 (8)		
			O(4)—Ca(1)—O(5)	69·8 (2)	O(1)	O(6)	2·859 (8)		
			O(4)—Ca(1)—O(6)	93·6 (2)	O(2)	O(3)	2·798 (8)		
			O(4)—Ca(1)—O(7)	76·7 (2)	O(2)	O(6)	2·961 (10)		
			O(5)—Ca(1)—O(6)	114·0 (2)	O(3)	O(6)	2·965 (8)		
			O(5)—Ca(1)—O(7)	80·6 (2)	Al(2)	O(5)	1·772 (7)	O(5)—Al(2)—O(8)	106·5 (3)
			O(6)—Ca(1)—O(7)	158·9 (2)	Al(2)	O(8)	1·778 (7)	O(5)—Al(2)—O(8)′	106·5 (3)
Ca(2)	O(1)	2·298 (6)	O(1)—Ca(2)—O(3)	69·1 (2)	Al(2)	O(8)′	1·778 (7)	O(5)—Al(2)—O(9)	108·7 (5)
Ca(2)	O(3)	2·573 (7)	O(1)—Ca(2)—O(4)	140·1 (2)	Al(2)	O(9)	1·727 (9)	O(8)—Al(2)—O(8)′	109·1 (5)
Ca(2)	O(4)	2·318 (5)	O(1)—Ca(2)—O(6)	85·9 (2)		Mean	1·768	O(8)—Al(2)—O(9)	112·9 (3)
Ca(2)	O(6)	2·363 (6)	O(1)—Ca(2)—O(7)	128·1 (2)				O(8)—Al(2)—O(9)	112·9 (3)
Ca(2)	O(7)	2·570 (7)	O(1)—Ca(2)—O(9)	89·9 (2)					
Ca(2)	O(9)	2·283 (7)	O(3)—Ca(2)—O(4)	92·8 (2)	O(5)	O(8)	2·844 (8)		
	Mean	2·401	O(3)—Ca(2)—O(6)	139·6 (3)	O(5)	O(8)′	2·844 (8)		
			O(3)—Ca(2)—O(7)	75·3 (2)	O(5)	O(9)	2·843 (12)		
			O(3)—Ca(2)—O(9)	127·3 (3)	O(8)	O(8)′	2·896 (12)		
			O(4)—Ca(2)—O(6)	86·7 (2)	O(8)	O(9)	2·921 (10)		
			O(4)—Ca(2)—O(7)	76·1 (2)	O(8)′	O(9)	2·921 (10)		
			O(4)—Ca(2)—O(9)	127·6 (2)					
			O(6)—Ca(2)—O(7)	142·4 (2)	Al(3)	O(4)	1·753 (6)	O(4)—Al(3)—O(4)′	107·0 (4)
			O(6)—Ca(2)—O(9)	81·8 (2)	Al(3)	O(4)′	1·753 (6)	O(4)—Al(3)—O(5)	98·2 (3)
			O(7)—Ca(2)—O(9)	82·8 (2)	Al(3)	O(5)	1·779 (8)	O(4)—Al(3)—O(7)	118·8 (3)
Ca(3)	O(2)	2·451 (9)	O(2)—Ca(3)—O(6)	133·3 (2)	Al(3)	O(7)	1·743 (9)	O(4)′—Al(3)—O(5)	98·2 (3)
Ca(3)	O(6)	2·485 (7)	O(2)—Ca(3)—O(6)′	133·3 (2)		Mean	1·757	O(4)′—Al(3)—O(7)	118·8 (3)
Ca(3)	O(6)′	2·485 (7)	O(2)—Ca(3)—O(8)	84·8 (3)				O(5)—Al(3)—O(7)	112·1 (5)
Ca(3)	O(8)	2·623 (7)	O(2)—Ca(3)—O(8)′	84·8 (3)					
Ca(3)	O(8)′	2·623 (7)	O(2)—Ca(3)—O(9)	98·7 (4)	O(4)	O(4)′	2·818 (12)		
Ca(3)	O(9)	2·352 (9)	O(6)—Ca(3)—O(6)′	92·1 (3)	O(4)	O(5)	2·669 (8)		
	Mean	2·503	O(6)—Ca(3)—O(8)	123·2 (2)	O(4)	O(7)	3·009 (8)		
			O(6)—Ca(3)—O(8)′	75·7 (2)	O(4)	O(5)	2·669 (8)		
			O(6)—Ca(3)—O(9)	77·9 (2)	O(4)	O(7)	3·009 (8)		
			O(6)′—Ca(3)—O(8)	75·7 (2)	O(5)	O(7)	2·922 (12)		
			O(6)′—Ca(3)—O(8)′	123·2 (2)					
			O(6)′—Ca(3)—O(9)	77·9 (2)	Al(4)	O(1)	1·778 (5)	O(1)—Al(4)—O(3)	104·6 (3)
			O(8)—Ca(3)—O(8)′	67·0 (3)	Al(4)	O(3)	1·764 (6)	O(1)—Al(4)—O(4)	105·3 (3)
			O(8)—Ca(3)—O(9)	146·4 (2)	Al(4)	O(4)	1·786 (7)	O(1)—Al(4)—O(8)	112·8 (3)
			O(8)′—Ca(3)—O(9)	146·4 (2)	Al(4)	O(8)	1·735 (7)	O(3)—Al(4)—O(4)	105·5 (3)
						Mean	1·766	O(3)—Al(4)—O(8)	117·9 (4)
								O(4)—Al(4)—O(8)	109·8 (3)
					O(1)	O(3)	2·803 (8)	Al(1)—O(1)—Al(4)	120·7 (3)
					O(1)	O(4)	2·834 (8)	Al(1)—O(2)—Al(1)	136·7 (7)
					O(1)	O(8)	2·926 (9)	Al(1)—O(3)—Al(4)	111·0 (4)
					O(3)	O(4)	2·825 (9)	Al(2)—O(8)—Al(4)	117·0 (4)
					O(3)	O(8)	2·997 (9)	Al(2)—O(5)—Al(3)	136·5 (6)
					O(4)	O(8)	2·880 (9)	Al(3)—O(4)—Al(4)	120·4 (3)

consideration of the interatomic distances between the members of the two different sets.

The positions of the remaining Ca and Al atoms in the asymmetric unit were located in electron density maps computed with the phases of the two Ca atoms (z coordinates relative to the fixed coordinate of one Ca atom used to define the origin of the unit cell). A further map computed with the phases of all the cations revealed the sites of the O atoms. 16 atoms in the asymmetric unit were found of which 2Ca, 2Al and 5O lie in equipoint position 8(b) and 1Ca, 2Al and 4O in position 4(a).

The structure was refined by least squares, the function minimized being $w(|F_o|-G|F_c|)^2$. The weights, w, were calculated from $w = 1/(40 + |F_o| + 0.005 \times |F_o|^2 + 0.00007|F_o|^3)$, based on the method proposed by Cruickshank (1965), and gave reasonably constant averages of $w\Delta F^2$ with $|F_o|$ and $(\sin \theta)/\lambda$ at the end of refinement. 136 parameters were refined simultaneously; all atoms were refined with anisotropic temperature factors and the 14 scale factors, corresponding to the individual layers of data, were refined independently of data set. The refinement converged to an R of 0.098 with an average parameter shift/e.s.d. of less than 0.1. Scattering factors were taken from Hanson, Herman, Lea & Skillman (1964) for neutral Ca, Al and O.

From an analysis of polar dispersion errors in the refined z coordinates of the Ca atoms, arising from the neglect to correct the data for anomalous dispersion effects (Cruickshank & McDonald, 1967), it was considered unlikely that the inclusion of the imaginary component of the anomalous dispersion term for Ca would significantly affect the Ca—O distances. Refinement with the inclusion of such terms was therefore not carried out.

The positional parameters of the atoms and important interatomic bond lengths and angles are given in Tables 1 and 2 respectively.* The computations were made on the University of London CDC6600 computer with programs from the Birkbeck College Crystallographic Program Library.

Description and discussion of the structure

The structure of $5CaO.3Al_2O_3$, illustrated in Figs. 1 and 2, consists of alternating twisted sheets of distorted AlO_4 tetrahedra and layers of Ca atoms which lie approximately perpendicular to [001]. The tetrahedra are linked through corners to form a network of
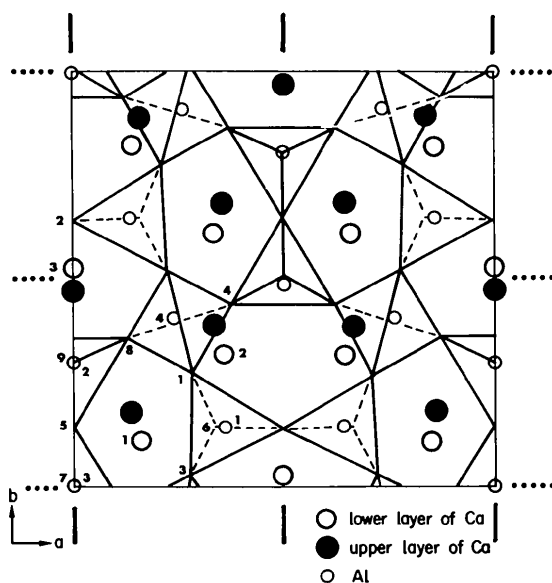
* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33253 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Fig. 1. Part of the structure of $5CaO.3Al_2O_3$ projected on (001). Only one layer of tetrahedra, which lies between the two Ca layers, is shown for clarity. The relative orientation of the second layer with respect to the first may be seen in Fig. 2. The atoms in the asymmetric unit are identified (corners of tetrahedra representing O atoms). Where ambiguity exists between Al and O identities due to the projection, the numbers on the *left* of the overlapping sites refer to Al. The positions of the symmetry elements are indicated by thick lines (mirror planes) and dotted lines (c-glide planes).
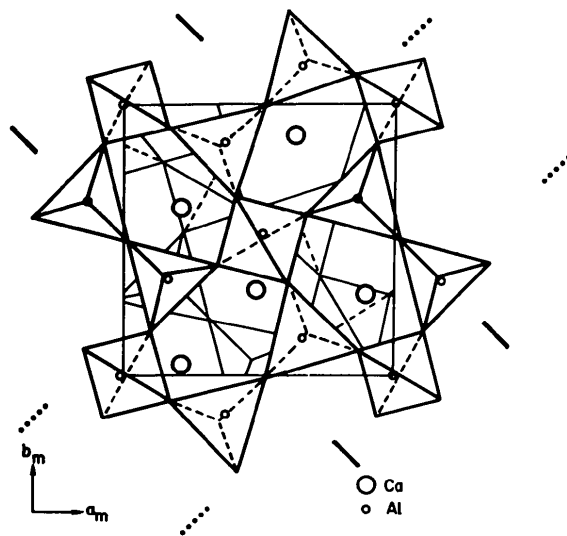

Fig. 2. Part of the structure of $5CaO.3Al_2O_3$ based on the primitive monoclinic subcell projected on (001). The origin has been shifted to lie at Al(4) in the upper layer of tetrahedra. Only one layer of Ca atoms, which lies between the two layers of tetrahedra, is shown. Symmetry elements are indicated in the same manner as in Fig. 1.

five-membered rings. A comparison of Figs. 1 and 2 with Fig. 3 shows that, in general, the structural features are essentially the same as those found in gehlenite ($P\bar{4}2_1m$: $a = 7\cdot717$, $c = 5\cdot086$ Å, Raaz, 1930; Louisnathan, 1970).* It follows that $5CaO.-3Al_2O_3$ provides no other basis from which the structures of the quaternary and ternary compounds, mentioned in the *Introduction*, can be determined, thus verifying the conclusion of Majumdar (1964).

Fig. 2, based on the primitive monoclinic subcell deduced from the centred orthorhombic cell ($a_m = b_m = 7\cdot856$, $c_m = 10\cdot290$ Å, $\gamma_m = 91\cdot48°$ where $a_m = \frac{1}{2}a_o + \frac{1}{2}b_o$, $b_m = \frac{1}{2}b_o - \frac{1}{2}a_o$, $c_m = c_o$, volume $V_m = \frac{1}{2}V_o$ and subscripts m and o refer to monoclinic and orthorhombic respectively), has been drawn so that the differences and similarities between the two structures can be seen.

Apart from the obvious similarities indicated in the two figures, it can also be shown that the point symmetries of the tetrahedral groups in $5CaO.3Al_2O_3$ approximate to their equivalents in gehlenite.

The major differences between the two structures are the relative orientations of consecutive sheets of tetrahedra (hence the doubling of c in $5CaO.3Al_2O_3$) and the number of Ca atoms for an equivalent number of O atoms; $5CaO.3Al_2O_3$ has an extra Ca atom per layer per monoclinic subcell in comparison with gehlenite.

The position of this extra Ca site can be seen from a

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* Louisnathan (1970) infers in his article that the space group $P\bar{4}2_1m$, to which the structure of gehlenite belongs, is polar. This is clearly incorrect.
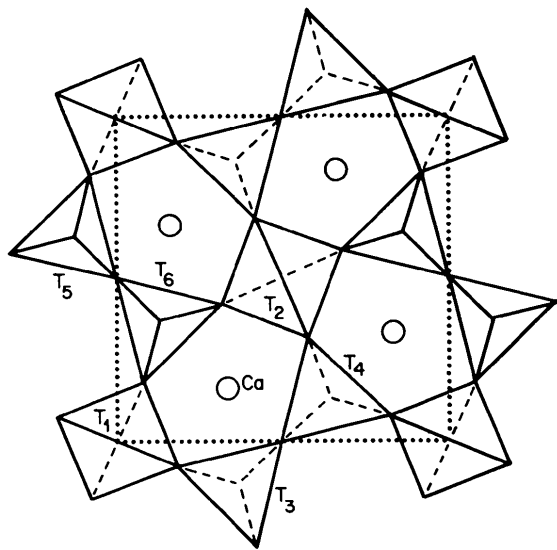
comparison of the two figures. Its introduction only severely affects the position of one Ca (with respect to the gehlenite structure) and therefore, in this sense, is apparently localized. Fig. 4 shows that the Ca(1) and Ca(2) polyhedra share a common face.

The Ca(1)–Ca(2) distance across this face is $3\cdot212$ Å while the Ca(2)–Ca(2)' distance across the mirror plane is $3\cdot200$ Å. A distance of $3\cdot267$ Å is also found between Ca(2) and Ca(1)' across a common edge. These distances, compared with the Ca–Ca distances in gehlenite (all $3\cdot547$ Å),* represent very short contacts and as a result, and considering there are no shielding effects between the Ca atoms, it may be thought that there is a certain amount of stress due to electrostatic repulsion in the structure. In fact Aruja (1957) has noted that crushing specimens into smaller fragments causes distortions, judged from the character of powder lines in a powder pattern. It may be concluded therefore that there is a direct correlation between the environmental conditions of the Ca atoms and the observations of Aruja. Furthermore, if it is considered that the Ca atoms are in an unstable situation then the metastable state of this compound may be at least partially explained.

In an attempt to account for the variations in oxygen–cation distances, an examination of the bond strengths at each O atom following the Pauling (1929)–Zachariasen (1963) method of the balancing of valences was made (Pant & Cruickshank, 1967; Pant, 1968). By assigning bond strengths of $\frac{3}{4}$ to tetrahedral Al–O bonds and $\frac{1}{3}$ to Ca–O bonds (assuming that all Ca atoms are six-coordinated), the total contribution

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* All other Ca–Ca distances in $5CaO.3Al_2O_3$ are greater than this.

Fig. 3. The gehlenite structure projected on (001). T_1 and T_2 are pure AlO_4 tetrahedra, while the tetrahedra T_3–T_6 have an occupancy of $Al_{0.5}Si_{0.5}$ (after Louisnathan, 1970).

Table 3. *Cation coordination of the O atoms with estimated bond valencies* (v.u.)

Oxygen	Total bond strength	Cation coordination (bond lengths in Å)			
O(1)	2·17	Ca(1) (2·292)	Ca(2) (2·298)	Al(1) (1·766)	Al(4) (1·778)
O(2)	1·83	Ca(3) (2·451)	Al(1) (1·727)	Al(1)' (1·727)	
O(3)	2·17	Ca(1) (2·584)	Ca(2) (2·573)	Al(1) (1·810)	Al(4) (1·764)
O(4)	2·17	Ca(1) (2·354)	Ca(2) (2·318)	Al(3) (1·753)	Al(4) (1·786)
O(5)	2·17	C(1) (2·310)	Ca(1)' (2·310)	Al(2) (1·772)	Al(3) (1·779)
O(6)	1·75	Ca(1) (2·302)	Ca(2) (2·363)	Ca(3) (2·485)	Al(1) (1·747)
O(7)	2·08	Ca(1) (2·507) Ca(1)' (2·507) Ca(2) (2·570) Ca(2)' (2·570) Al(3) (1·743)			
O(8)	1·83	Ca(3) (2·623)	Al(2) (1·778)	Al(4) (1·735)	
O(9)	1·75	Ca(2) (2·283)	Ca(2)' (2·283)	Ca(3) (2·352)	Al(2) (1·727)

from each cation to each O atom could be determined (Table 3).

Comparison of the Al—O lengths for the overbonded O atoms [O(1), O(3), O(4), O(5) and O(7)] with those of the underbonded O atoms [O(2), O(6), O(8) and O(9)] shows that, in general, the shorter Al—O distances are associated with underbonded and the longer Al—O distances with overbonded O atoms. One notable exception is the bond between Al(2) and the underbonded O(8), whose length is similar to those found for the overbonded O—Al distances.

If the π-bonding model proposed by Cruickshank (1961) as summarized by Brown, Gibbs & Ribbe (1969) is applicable to Al—O bonds in AlO_4 (tetrahedral) groups then, from the prediction that 'the length of the Al—O bond to non-bridging oxygens should be shorter than the bond to bridging oxygens', it is found that the deviations from this model can be accounted for by the Pauling—Zachariasen method and vice versa. In fact, according to Pant (1968) such a situation may exist since π-bonding may be part of the mechanism whereby valency balance is achieved.

A similar comparison made between the Ca—O lengths for the overbonded and underbonded O atoms shows that the pattern of longer bonds being associated with overbonded and shorter bonds with underbonded O atoms is not consistently obtained. In particular, the

Fig. 4. Illustration of the environments of the Ca atoms and the sharing of polyhedral elements in the structure of $5CaO.3Al_2O_3$ as viewed down [001]. The numbers at the corners of polyhedra define O atoms. Symmetry elements are indicated in the same manner as in Fig. 1.

overbonded O(1) and O(5) have some of the shortest Ca—O distances whereas the underbonded O(8) has one of the longest.

Zachariasen (1963) has pointed out that nextnearest-neighbour interactions also affect the bond lengths and therefore the method of balancing of valences cannot be expected to account for all observed bond-length anomalies. Consideration of these factors, however, does lead to possible explanations for some of the anomalies mentioned above.

Fig. 4 shows that the Ca(1)' and Ca(2) octahedra have a common face, defined in the diagram by O(3), O(4) and O(7). The faces defined by O(1), O(5) and O(6) of the Ca(1)' octahedron, and O(1)', O(6)', and O(9)' of the Ca(2) octahedron are opposite to this face. The positions of the Ca atoms in relation to these faces are such that Ca(1)' is nearer to the face O(1)—O(5)—O(6) and Ca(2) to the face O(1)'—O(6)'—O(9)' than either is to the common face O(3)—O(4)—O(7). If the positions of the O atoms can be assumed to be fixed by virtue of the strong Al—O bonds, then the mutual electrostatic repulsion between Ca(1)' and Ca(2) would cause their positions to be closer to the faces O(1)—O(5)—O(6) and O(1)'—O(6)'—O(9)' respectively. This reasoning would explain the short bonds Ca(1)—O(1) and Ca(1)—O(5). It also holds for the other variations in Ca(1)—O and Ca(2)—O lengths found in the structure.

If Ca—O distances of 3·1 Å are considered as bonds (Megaw, Kempster & Radoslovich, 1962) then Ca(3) will be, by symmetry, additionally bonded to two O(3) atoms [3·032 (7) Å] with, perhaps, Ca(1) bonded to O(8) [3·132 (7) Å] and also Ca(2) to O(8) [3·166 (8) Å]. In the former case only the bond strength at O(3) is substantially altered, resulting in no change in the correlation already found between bond strength and bond distances for this atom. On the other hand, the bond strength at O(8) is increased such that it changes its character from underbonded to overbonded by the inclusion of either one or both of these extra bonds. From the point of view of the method of balancing valences, such inclusions would provide a better fit between bond strength and the associated bond lengths for this O atom.

Finally, it would be of interest if a possible explanation could be found for the localized manner in which the extra Ca atoms affect the sites of the remaining Ca atoms in $5CaO.3Al_2O_3$ as compared to the gehlenite structure.

By neglecting the contributions from the Ca atoms in the determination of the total charges at the O atoms, O(6), O(7) and O(9) have partial strengths of 0·75 while the remainder have values which are twice as great. Thus it may be expected that these three O atoms would attract Ca atoms more strongly than the others because of their much larger deviations from charge neutrality. It will be seen in Fig. 4 that O(6), O(7) and
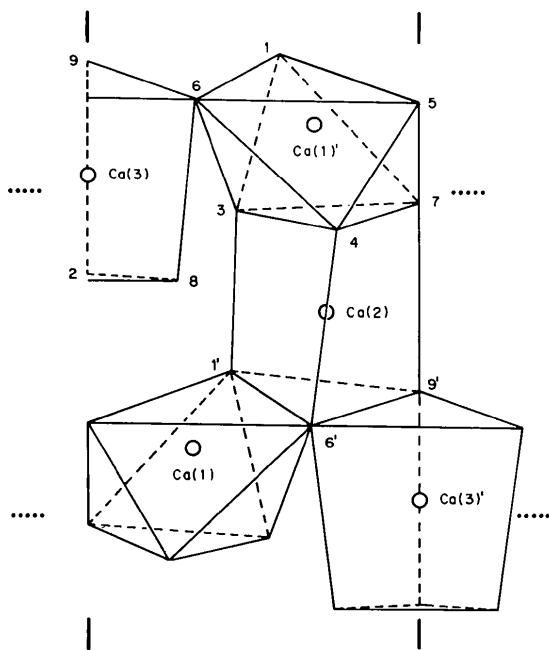
O(9) are part of the Ca(2) oxygen coordination polyhedron and that O(7) and O(9) form the common edge between two Ca(2) polyhedra. Since the two Ca atoms across this edge are the ones in question, it may be concluded from the positions and partial bond strengths of these O atoms that an explanation exists within the limitations of the model adopted here.

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The Crystal Structure of 4Na₂SO₄.2H₂O₂.NaCl

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The structure of $4Na_2SO_4.2H_2O_2.NaCl$ has been refined to $R = 0.071$. The unit cell is tetragonal [$a = 10.53$ (1), $c = 8.42$ (1) Å] and there exists a supercell with an a and b repeat four times larger than the basic cell used for the structure determination. The H_2O_2 molecules appear to have orientational disorder but this is only a consequence of using the smaller cell: they are held within infinite tunnels (parallel to c) by hydrogen bonds to O atoms of the sulphate groups. The coordination around eight of the Na^+ ions is distorted octahedral, whereas around the other there is a regular eightfold coordination with tetragonal-prismatic symmetry.