Tafel 5.3.6A der *International Tables* ersichtlich ein Übertragungsfehler eingeschlichen, der leider auch Folgefehler in der Tabelle 5.3.6B verursacht hat. Die übrigen Abweichungen, welche die Tabelle 1 erkennen lässt, sind dagegen gering; ihre Ursache darf wohl in erster Linie restlichen numerischen Ungenauigkeiten der Tabellen 5.3.6A zugeschrieben werden.

Ein Beispiel für eine erweiterte Anwendung der A_{Kug}-Tabelle

Es sei bemerkt, dass man mit der Schreibweise (4) des Absorptionsfaktorintegrals implizit auch einen wichtigen speziellen elliptischen Fall erfasst, nämlich den Fall des Rotationsellipsoids dessen Rotationssymmetrieachse **c** die Drehachse ist und das $\perp$**c** durchstrahlt wird (sogen. Äquatoraufnahme). Führt man vor der Substitution (3) eine lineare Dehnung in z-Richtung durch

$$z \rightarrow z' = (c/a)z$$

so wird die Kugel in ein Rotationsellipsoid mit den Achsen $a = R$ und $c = (c/a)R$ überführt; a wie r bleiben von der Dehnung unberührt, da sie senkrecht zur Dehnungsrichtung liegen. Man findet:

$$A_{\mathrm{Ell}} = \int_{-1}^{+1} r^2 \pi A_{\mathrm{Zyl}}(\mu r) dz' / (4\pi a^2 c/3)$$

$$= \tfrac{3}{4} \int_{-1}^{+1} \left(\frac{r}{a}\right)^2 A_{\mathrm{Zyl}}(\mu r) \frac{(c/a)dz}{(c/a)a},$$

das unter Beachten der Substitutionen (3) und nach Kürzen von Zähler und Nenner unmittelbar in (4) übergeht:

$$A_{\mathrm{Ell}} = A_{\mathrm{Kug}}(\mu a) .$$

Diese Gleichung besagt, dass der Absorptionsfaktor A_{Ell} des Rotationsellipsoides bei einer Durchstrahlung $\perp$**c** unabhängig von der Länge der c-Achse ist und mit dem Wert A_{Kug} für $R = a$ übereinstimmt (Weber, 1963).

Der Verfasser dankt der Deutschen Forschungsgemeinschaft auch an dieser Stelle vielmals für die finanzielle Unterstützung der vorliegenden Arbeit. Dank gebührt ferner dem Deutschen Rechenzentrum, mit dessen IBM-Anlage 7094 alle vorliegenden numerischen Berechnungen ausgeführt werden konnten.

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A System for the Coding and Generating of Layered, Tetrahedrally Close-Packed Structures

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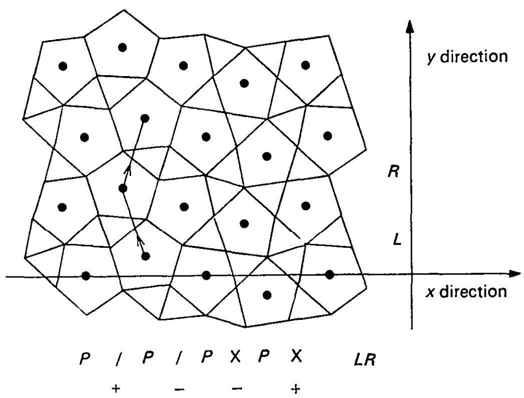
A simple coding system is proposed which applies to those layered, tetrahedrally close-packed structures whose secondary nets may be generated by two sets of parallel (zigzag) lines (β-W, Friauf–Laves, μ, σ, P, M phases, *etc.*). This coding scheme represents a great condensation of structural data, from which atomic coordination can be regenerated; it enables one to recognize similarities between structures without plotting out all the atoms; and it indicates how new members of this structure family may be generated.

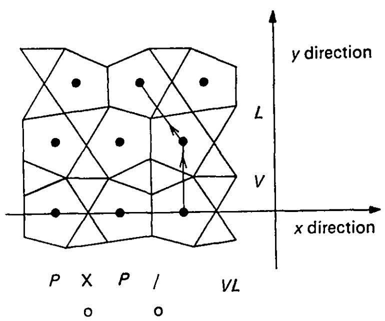
Introduction

Tetrahedrally close-packed structures (Frank & Kasper, 1958, 1959; Shoemaker & Shoemaker, 1967, 1969) contain interpenetrating triangulated coordination number (CN) 12, 14, 15, or 16 polyhedra which are in most cases generated by the alternate stacking of primary layers of pentagon-triangle, pentagon-hexagon-triangle or hexagon-triangle nets of atoms with secondary layers of triangle, square-triangle or square nets of atoms, such that all pentagons of successive primary nets are covered antisymmetrically by pentagons of neighbouring primary nets, and similarly for the hexagons. The atoms of the secondary interleaving nets

centre all (and only) the pentagons and/or hexagons of the primary nets. There are also some tetrahedrally close-packed structures that are not formed by stacking planar layers; for instance the R and δ phases. In these cases there are regions where the atoms are almost confined to planes as in the layered structures, but there are also regions where the planarity is disturbed. The generating and coding only applies to the layered, tetrahedrally c.p. structures. It is convenient to regard such structures in two groups: (1) those characterized by a linear repeat sequence of pentagons and/or hexagons along what we call the basal repeat row, such that repetition of this sequence along the row and about a direction normal to the basal row generates the whole of the primary net. The structures in this group are characterized by a secondary net that may be generated by two sets of parallel (in most cases zigzag) lines; (2) those structures whose secondary nets cannot be generated by two sets of parallel (zigzag) lines. In some cases these structures may be characterized by having a two-dimensional tile of pentagons and/or hexagons, which by repetition generates the whole net as in the case of Fig. 16 of Frank & Kasper (1959).



(a)



(b)

Fig. 1(a). Structure diagram and code for the M phase (Nb–Ni–Al). (b) Structure diagram and code for the μ phase (Mo_6Co_7). Atoms of one primary net at intersections of lines, atoms of secondary net represented by full circles. Second primary net which covers pentagons of first primary net antisymmetrically is not shown.

In both groups successive primary nets whose pentagons and/or hexagons severally cover those of the preceding net antisymmetrically may or may not be equivalent.

An essentially unlimited number of possible structures of both groups can be devised; whereas group 2 structures are currently recognized only as rarities in our appreciation of structural architecture, those of group 1 are well-known in such phases as Laves, σ, μ, P, M, *etc.*, and an increasing number of structures are being attributed to this class. Frank & Kasper (1958, 1959), who developed our systematic knowledge of these structures, proceeded heuristically deriving different codings to describe different families of structures. However, as a result of subsequent work (notably Shoemaker & Shoemaker, 1967, 1969) it is apparent that *all* structures of group 1 can be described systematically by coding the repeat sequence of pentagons and/or hexagons of the primary net along two orthogonal axes X and Y. Since pentagons and hexagons of one primary net are covered antisymmetrically by those of primary nets above and below, these are also defined by the coding of the first primary net, as is the secondary net whose atoms centre pentagons and hexagons (only) of the primary net.

Coding of structures whose primary nets have linear (zigzag) repeat units

Symbols describe the pentagons (P) and hexagons (H) in the primary layers and the method of joining these, either edge to edge (/) or apex to apex with two intervening triangles (×). The nets are oriented with respect to the orthogonal X and Y axes such that the X axis (horizontal) gives the direction of extension of the basal row of polygons sharing apices and/or edges, and the Y axis (vertical) makes an angle between 0° and approximately 30° with the direction in which the basal row repeats itself in the same orientation. The next row is not necessarilly a crystallographic repeat of the first one, but it contains pentagons and hexagons in the same sequence and orientation. The repeat sequence of pentagons and/or hexagons along the X direction can be described with these symbols as, for example, $P/P/P\times P\times$ for the M phase structure [(Fig. 1(a)].

The connections between pentagons or hexagons may cause the row to continue in a direction up (coded +) or down (coded −) with respect to the X direction or in a direction parallel to it (coded 0). The basal row should extend in the direction of the X axis, that is the kinks should always produce turns towards the X axis, or if a turn is away from the X axis, the next turn should be towards it. Thus the repeat sequence for the M phase is $P/P/P\times P\times$.
+ − − +

The basal repeat unit of the primary net repeats along the orthogonal Y direction with shift movements either left (symbol L), or right (symbol R) or none

(symbol *V*), so that the pentagons and/or hexagons form strips in this direction. Along these strips hexagons are connected either by opposite edges or apices (continuing the direction *L*, *R* or *V*) or by an edge and a next-but-one apex or by two next-but-one edges or apices, (changing the direction from *L*, *R*, or *V*). Successive pentagons along these strips share one apex *with an intervening triangle on one side* (See *e.g.* Fig. 1).

Repetition of the repeat unit along the basal row and along the *Y* axis according to its repeat scheme generates the whole of the primary net. Since the pentagons and hexagons of one primary net are covered antisymmetrically by pentagons and hexagons of the primary nets above and below, specification of the basal repeat of one primary net gives the primary nets above and below merely by interchanging × for / and *vice versa;* the repeat sequence along the *Y* axis remains unchanged. Thus, for example, the primary nets above and below the primary net $H\times P/H\times P/;\ LR$ ($+\ +\ -\ -$) are $H/P\times H/P\times;\ LR$ ($+\ +\ -\ -$). This indicates that in the approximate direction of the *X* axis successive polyhedra (icosahedra or CN14 polyhedra) share triangular faces. In the approximate direction of the *Y* axis CN14 polyhedra also share triangular faces, *but icosahedra share edges.*

Since all of the atoms of the secondary net centre all the pentagons and/or hexagons of the primary nets (not the triangles), the designation of the primary net repeat sequence specifies also the secondary net, and therefore the location, sequence and coordination of all atoms in the structure. Primary net sequences (0; *LR*) give 3^6 (Schläfli symbol) secondary nets, (0; V) give 4^4 secondary nets and (+ −; *LR*, *etc.*) or (0; *VL*, *etc.*) or 0; *VR*, *etc.*) give square-triangle secondary nets.

This system of coding enables one to describe very simply any group 1 tetrahedrally close-packed structure having a linear (zigzag) basal repeat sequence, in such a way that the structural arrangement of the primary and secondary nets can be generated from the symbols, and the coordination of the atomic sites recognized. It therefore permits a very great condensation of structural information, as well as the systematic prediction of all possible structures of this type. It is only necessary to generate the primary net (both primary nets in case they are non-equivalent) in order to determine the coordination of the various atoms. This is uniquely fixed by the type of connections between pentagons and/or hexagons; all possible cases for group 1 structures are shown in Fig. 2.

In Table 1 codes for some group 1 structures are given arranged in three subgroups to facilitate generation of other possible structures. Under *A* are listed structures with + and − in the horizontal row and *L* and/or *R* in the vertical direction. The secondary net consists of squares and triangles and all kinks in the parallel lines are about 150°. New structures may be generated by changing the sequence of + and −, or for a certain + − sequence by changing the sequence of *H* and *P*, making sure that there is an even number of kinks (including in the count the kink that may be introduced at the end of the sequence) in order to produce a repeat. More structures result from changing the *LR* sequence for each + −, *HP* sequence.

The structures listed under *B* in Table 1 are characterized by 0 in the horizontal row and *L*, *R* or *V* in the vertical direction. *V* followed by *L* or *R* produces 150°

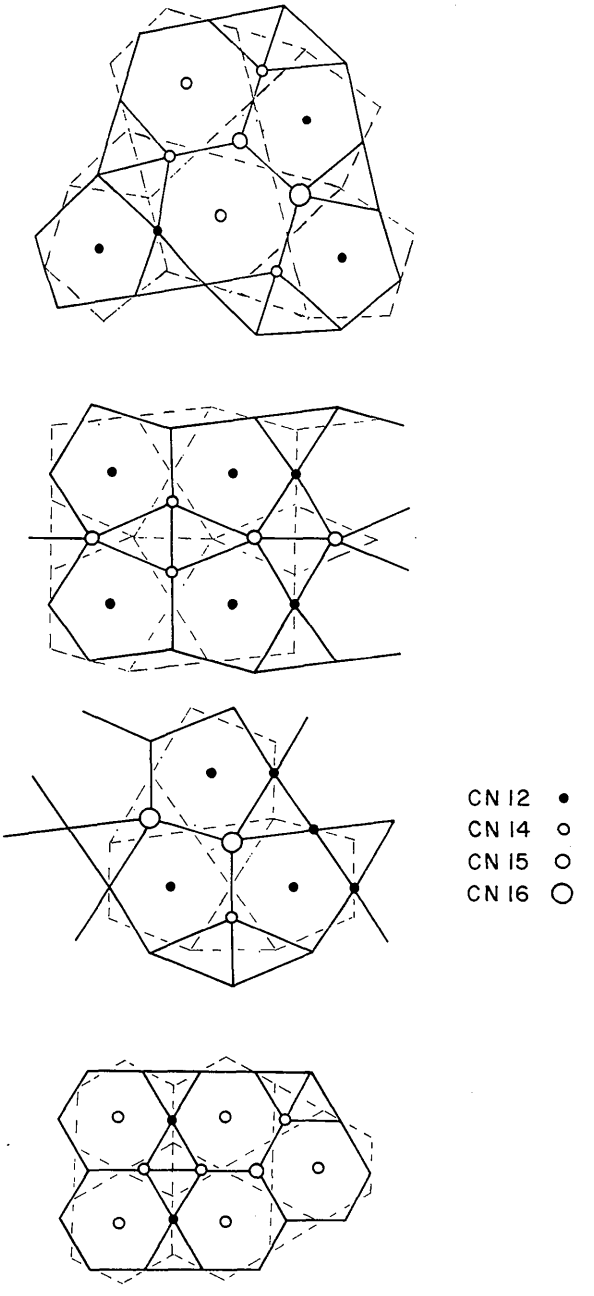


Fig. 2. Atom coordinations in layered, tetrahedrally close-packed structures. The second primary net is shown in broken lines.

kinks as above, but L followed by R (and *vice versa*) produces 120° kinks. With only V the secondary net is rectangular, with only L followed by R (and *vice versa*) it is triangular. There is now a fundamental difference between all-H and all-P structures. Since in the case of all-H L and R result in the same row sequence, there is only one all-H structure with triangular net (Zr_4Al_3 down the hexagonal axis). In the case of an all-P structure L and R represent different row sequences. Each pentagon is adjacent to two pentagons in the next row, sharing an apex or side with one of them (icosahedra sharing a face) and an apex with intervening triangle on one side with the other (isosahedra sharing an edge). As explained above, the strips are chosen in the latter directions. The different Friauf–Laves phases all have topologically the same secondary net but differ in L R sequences. In H–P structures L and R are naturally different. In the sequence along the row each polygon may be again H or P as long as a repeat is achieved and in vertical direction new structures may be formed by different sequences of L, R and V.

In the structures of types A and B the basal rows are chosen such that a hexagon shares either opposite apices (or edges: no change of direction) or one edge and one non-adjacent apex (change of direction). Similarly, a pentagon shares an edge and an opposite apex (no change of direction) or two non-adjacent edges (or apices: change of direction). In some cases, examples of which are listed under C in Table 1, there is an alternate choice of basal row [shown in Fig. 3(*a*) for $MgCu_2$] which results in a unit cell with a small rectangular repeat. The structure has a mirror plane perpendicular to the plane of the paper containing the X' direction. A row line making an angle with the X' direction may, therefore, be called $\pm$. A kink of about 150° is produced by $\pm$ followed by 0; a kink of about 120° results from $\pm$ followed by $\mp$ (pentagon sharing an edge and adjacent apex or hexagon sharing two next-but-one edges or apices). In order to maintain parallel rows along the Y' axis only V is allowed in that direction. The structures derived by different combinations of $\pm$ and 0, may also be derived by the procedures described above and no new structures result.

Table 1. *Coding for some group* 1 *structures*

Structure	Planes in which nets lie	Coding for structure		Simplified code	Schläfli symbols for secondary net and ratio of numbers of different corners
A. σ phase	001	$H\times H/$ (+ −)	LR	$H(11; LR)$	3^2434
M phase	001	$P/P/P\times P\times$ (+ − − +)	LR	$P(22; LR)$	$3^2434+3^342(1/1)$
P phase	001	$P/H\times P/H\times$ (+ − − +)	LR	$PH(22; LR)$	$3^2434+3^342(1/1)$
Fig. 3(*b*)		$P/H/P/$ (− − +)	L	$PHP(21; L)$	$3^342+3^6(2/1)$
B. β-W	001	$H\times$ (0)	V	$H(0; V)$	4^4
Zr_4Al_3	110	$P\times P/$ (0 0)	V	$P(0; V)$	4^4
Zr_4Al_3	001	$H\times$ (0)	L, R	$H(0; L, R)$	3^6
$MgZn_2$	110	$P\times P/$ (0 0)	LR	$P(0; LR)$	3^6
$MgCu_2$	$1\bar{1}0$	$P\times P/$ (0 0)	L^3*	$P(0; L)$	3^6
$MgNi_2$	110	$P\times P/$ (0 0)	$LLRR$	$P(0; L^2R^2)$	3^6
MgAlCu (5-layer Laves)	110	$P\times P/$ (0 0)	L^4R	$P(0; L^4R)$	3^6
MgAlCu (9-layer Laves)	110	$P\times P/$ (0 0)	$(LLR)^3$*	$P(0; L^2R)$	3^6
μ phase	110	$P\times P/$ (0 0)	$(VL)^3$*	$P(0; VL)$	3^342
Idealized planar R		$P\times H\times P/H/$ (0 0 0 0)	$(VL)^3$*	$PH(0; VL)$	3^342
C. Alternate description for $MgCu_2$		$P\times P/$ ($\pm$ $\mp$)	V	$P(\pm\mp; V)$	
Alternate description for Fig. 3(*b*)		$P/H/P/$ ($\pm$ $\mp$ 0)	V	$PHP(\pm\mp 0; V)$	

* Tripling to achieve rectangular repeat.

This new axial system seems however promising in deriving group 2 structures. (For instance Frank & Kasper's hypothetical structure, shown in Fig. 16 of their 1959 paper, could be coded: $H\times H/H\times$, hexagonal.)
$\pm\ 0\ \mp$

There are some other features of the coding which are not uniquely defined, and this allows a choice in describing some structures, without impairing the usefulness of the coding, since the regeneration of the structure from the code adopted is indeed unique.

(1) The choice of primary and secondary nets is not necessarily uniquely defined. This is shown in Table 1 for the Al_3Zr_4 structure which can be described in two different projections, one with a 4^4 and the other with a 3^6 secondary net.

(2) When the primary net contains only *hexagons* (and triangles) either of the two orthogonal axes can be selected as the X direction. Thus, the 'all-hexagon μ' structure can be described either as $H/_0$; $V(L,R)$ or as $H/H\times_{-\ +}$; L. If similarity to the μ phase wants to be expressed the first description is the preferable one.

(3) When the primary net has a threefold symmetry axis as in the case of an all-H primary net with 3^6 secondary net there are, of course, three different choices for the basal row. When the structure has a mirror plane perpendicular to the plane of the nets so that the alternate description with a row line of type C is possible, there are also two choices for a basal row of type A: one all-R in vertical direction and the other one all-L [X'' and X in Fig. 3(*b*)].

The addition of the $+$, $-$ and 0 symbols to the coding is a redundant feature (if a row line of type C is left out of consideration), since the information is already contained in the sequence of $P,H,\times,/$ symbols; however, it does aid in viewing the repeat sequence of the primary and secondary nets. For typographical purposes the $+$, $-$, 0 and $\pm$ may be added as subscripts to the connection symbols $\times$ and $/$. For computer use these symbols might be printed on the same line after the connection symbols or, alternatively, be left out.

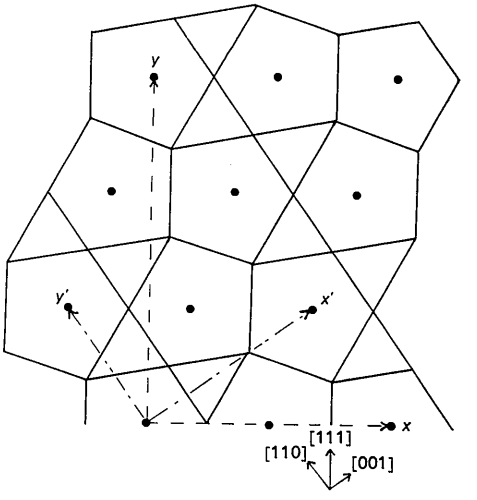
Comparison with Frank-and-Kasper symbols

Frank & Kasper (1959) developed a formalism for those planar, tetrahedrally close-packed structures which have a σ-phase type repeat in vertical direction (our type A structures with LR repeat, or type B structures with VL repeat). In Frank & Kasper's nomenclature the vertical σ-phase repeat is incorporated into their strips of pentagons and triangles or hexagons and triangles extending in the vertical direction. Depending on the way the polygons are tilted with respect to the vertical direction these strips are called D or U for pentagons (down and up) and L or R for hexagons (left and right). The strips are connected in a horizontal direction either directly (indicated by a period) or by an intervening triangle strip (indicated by p). Thus the symbol given for the P phase is:

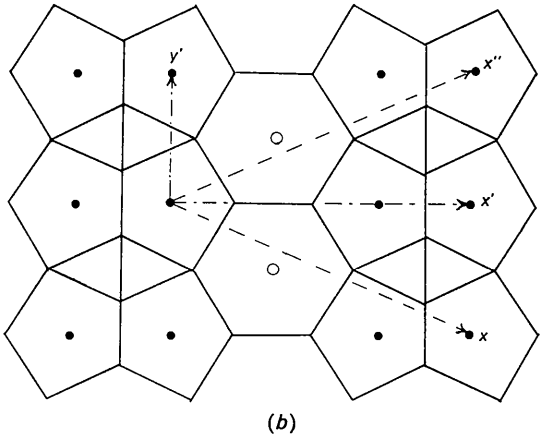
UpR.DpL.
$+\ -\ -\ +$ or numerical: (2,2).
D.LpU.Rp

Both primary nets are specified although the symbol for the second net follows directly from the first one. Our code for the basal row (Table 1) may be derived from this Frank & Kasper symbol by replacing U and D by P,L and R by H,p by $\times$ and(.) by $/$. To complete our code the sequence in the vertical direction (which may differ from the σ-phase sequence) has to be given also.

A different formalism was used by Frank & Kasper for those tetrahedrally close-packed structures which



(*a*)



(*b*)

Fig. 3(*a*). Primary and secondary net for $MgCu_2$, normal projection on $(1\bar{1}0)$. Alternate choice of unit cell is indicated. (*b*) Primary and secondary net for a hypothetical structure. Three possible choices for the X axis (direction of basal row) are indicated.

may be derived by stacking and in-filling of Kagomé nets perpendicular to a threefold axis, which includes the structures of the different types of Friauf-Laves phases. The symbol describing the layer sequence for $MgNi_2$ is: $\triangle\triangle\triangledown\triangledown$ and for the μ phase: $|\triangle 0|$. In our description the Kagomé nets are perpendicular to the plane of the paper containing the horizontal rows of secondary-net atoms. The Frank & Kasper symbols define our sequence in the vertical direction by replacing $\triangle$ by L, $\triangledown$ by R and 0 by V.

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The Crystal Sructure of Yugawaralite

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A single crystal of yugawaralite $Ca_2Al_4Si_{12}O_{32}.8H_2O$ was examined by X-rays and 1700 non-zero intensities were measured. An $N(z)$ test indicated the absence of a centre of symmetry and the space group Pc was adopted. Structural analysis has revealed an alumino-silicate framework consisting of 8-, 5- and 4-membered rings. In the course of the refinement the calcium cation appeared coordinated by four oxygen atoms and four water molecules, and aluminum and silicon were shown to be in an ordered arrangement from consideration of interatomic distances. With isotropic temperature factors the final reliability index was 0·065 and the $N(z)$ based on F_{calc} almost coincided with that of F_{obs}. Yugawaralite is a zeolite not belonging to any recognized family. It possesses a two-dimensional system of channels approximately $3{\cdot}6 \times 2{\cdot}8$ Å free diameter.

Introduction

Yugawaralite was described by Sakurai & Hayashi (1952) as a mineral of the zeolite family having the formula $Ca_4Al_7Si_{20}O_{54}14H_2O$ and a density of 2·20 g.cm^{-3}. More recently a crystal of yugawaralite found at Heinabergsjøkull, south-eastern Iceland, by Walker (1969) was used for further X-ray studies by Barrer & Marshall (1965). By means of Weissenberg and precession photographs they determined the unit cell as monoclinic with: $a = 6{\cdot}73 \pm 0{\cdot}01$ Å, $b = 13{\cdot}95 \pm 0{\cdot}01$ Å, $c = 10{\cdot}03 \pm 0{\cdot}01$ Å, $\beta = 111°30' \pm 2'$, giving unit-cell contents, with a certain degree of rounding, as $Ca_2Al_4Si_{12}O_{32}.8H_2O$. They applied the statistical test of Howells, Phillips & Rogers (1950), and the $N(z)$ plot suggested the absence of a centre of symmetry. From this and the noting of systematic absences they proposed the space group Pc. The structure has been briefly described by Kerr & Williams (1967); in the present paper a full and final description of the structure is given which includes the ordering of aluminum and silicon, and the cation and water positions.

Experimental

The present investigation is a continuation of that of Barrer & Marshall (1965) with a crystal of size $0{\cdot}2 \times 0{\cdot}2 \times 0{\cdot}2$ mm from the same source. A Buerger precession camera and Mo $K\alpha$ radiation were used for the systematic collection of three-dimensional X-ray intensity data. As it is not possible with a precession camera to use multiple film techniques, owing to the different angles of incidence of the two beams giving rise to the same diffraction spot, photographic data were obtained by taking a series of timed exposures of 27, 9, 3 and 1 hours and in some cases 20 minutes. The crystal was mounted so that it rotated about its b axis, thus enabling data to be collected up the two shorter axes without needing to remount the crystal. By use of a precession angle of 32·5° the following layers were taken: nkl where $n = 0, 1, 2$ and 3, and hkn where $n = 0, 1, 2, 3$ and 4.

A Joyce–Loebl integrating microdensitometer (of the flying spot scanner type) was used for measurement of all the data of about 6000 diffraction spots. It was found