

## Further detail on the crystal structure of zussmanite

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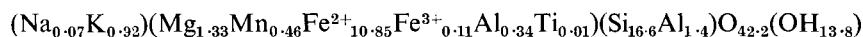
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SUMMARY. Mineral data and a brief outline of the structure for zussmanite (ideal formula

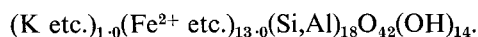


have been published previously. This paper describes the determination of the crystal structure and presents and discusses the results. The structure consists of rhombohedrally stacked layers of Fe-(O,OH) octahedra to each side of which are attached rings of six (Si,Al)-O tetrahedra. These composite layers are linked to one another by rings of three (Si,Al)-O tetrahedra, and by potassium atoms, the latter in positions analogous to those in a mica. There is some evidence of disorder of the layer stacking. Interatomic distances and angles, and valency balance, are discussed.

THE mineral zussmanite was discovered in 1960 by S. O. Agrell, along with two other new minerals, deerite and howieite, occurring in metamorphosed shales, siliceous ironstones and impure limestones of the Franciscan formation, Laytonville district, Mendocino County, California. A brief account by Agrell, Bown, and McKie (1965) described zussmanite as occurring in pale green tabular crystals with perfect cleavage, and gave the following further details: uniaxial with  $\omega$  1.645,  $\epsilon$  1.623; weakly pleochroic with  $\omega$  pale green and  $\epsilon$  colourless; specific gravity 3.146; rhombohedral  $R\bar{3}$  or  $R\bar{3}$  with  $a_{\text{hex}}$  11.66 Å,  $c_{\text{hex}}$  28.69 Å; formula from chemical analysis and on the basis of 56 oxygen atoms:



The above formula approximates very closely to



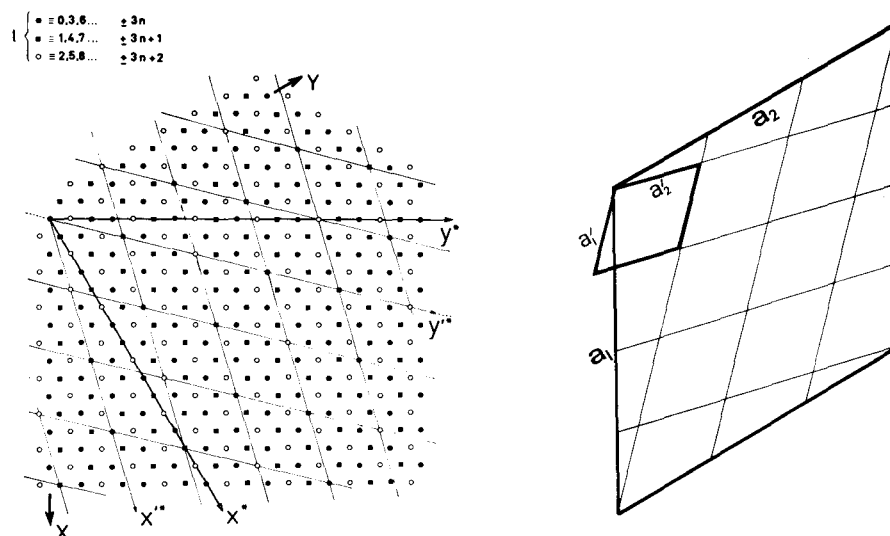
The structure of zussmanite has been determined, but has so far been described only in a short note (Lopes-Vieira and Zussman, 1967).

*Experimental.* The crystal used for the structure determination was a small rectangular plate measuring 0.16 × 0.14 × 0.06 mm. The crystal was mounted on a Weissenberg camera to rotate about an  $a_{\text{hex}}$  axis, and zero, first, second, and third layer reflections were recorded in equi-inclination settings. Zirconium-filtered molybdenum radiation was used, and reflections were recorded out to  $\sin \theta = 0.95$  for each layer. Intensities were measured visually by comparison with an intensity scale.

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Three unusual features of the X-ray photographs were noted: the presence of certain Weissenberg festoons of spots that were much stronger than average; the fact that many of the reflections were streaked parallel to  $c^*$ ; and the large proportion of possible reflections that were too weak to be observed (1156 observed and measured; 765 zero). Data reduction procedures were employed (absorption neglected) and  $|F|$  values were placed approximately on an absolute scale by the Wilson method.



FIGS. 1 and 2: FIG. 1 (left). Relationship in reciprocal space between true cell and sub-cell reflections. Zero and upper layer reciprocal lattice points are shown projected on to the  $hk0$  plane. True cell axes are  $x^*$  and  $y^*$ ; sub-cell axes are  $x'^*$  and  $y'^*$ ; the direct space true cell axes  $X$  and  $Y$  also marked. FIG. 2 (right). Relationship in direct space between the true cell  $a_1 \times a_2$  and the sub-cell  $a'_1 \times a'_2$  ('hexagonal' axes).

*Structure determination and results.* The structure of zussmanite was determined by the method of trial and error, since there were several good clues as to its nature. Physical properties and chemical composition both indicated a probable relationship to a mica; the shape and size of unit cell, and the presence of a set of very strong reflections corresponding to a much smaller pseudo-cell, both indicated further features of the structure.

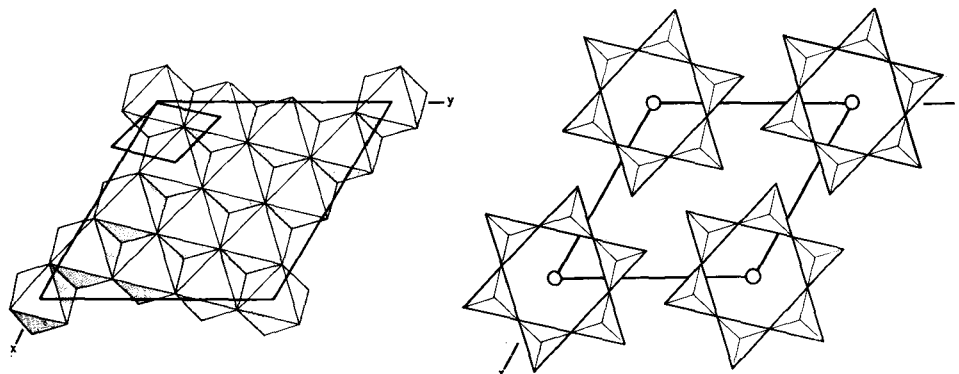
The particularly strong reflections were of the kind  $h.k.\overline{h+k}.l$  where  $k = 3h \pm 13n$  (where  $n = \text{integer}$ ). These reflections are shown in fig. 1, which is a plot of the reciprocal lattice projected on to  $(0001)$ . All reciprocal lattice points for the unit cell are shown, and the special reflections are seen to define a rhombohedral 'superlattice' in reciprocal space. The corresponding direct space relationships are shown in fig. 2, and numerical data are given in table I. If the iron atoms in zussmanite are assumed to lie in planes of Fe-(O,OH) octahedra similar to the Fe,Mg octahedra in biotite, then the dimensions and relative orientations of true cell and pseudo-cell can be derived as in fig. 3. This model of part of the structure had the further encouraging feature

that the unit (hex.) cell contained 13 Fe octahedra per layer of the structure, as required by the chemical formula.

It was therefore postulated that the entire structure consisted of rhombohedrally stacked layers of Fe-O octahedra, and that to either side of these there were attached (Si,Al)-O tetrahedra in such a way as to produce the unit cell repeat as shown in fig. 4. The presence of rings of six tetrahedra seemed likely because of the rhombohedral symmetry of the crystal lattice, and it was further assumed that the six-membered rings pointing opposite ways and attached to successive layers of octahedra

TABLE I. *Dimensions of true cell and sub-cell of zussmanite*

True cell: $a_h = 11.66 \text{ \AA}$ , $c_h = 28.69 \text{ \AA}$ ; rhombohedral true cell: $a_r = 11.69 \text{ \AA}$ , $\alpha_r = 59.8^\circ$ .
Sub-cell: $a'_h = 3.24 \text{ \AA} = a_h/\sqrt{13}$ , $c'_h = 28.69 \text{ \AA} = c_h$ ; rhombohedral sub-cell: $a'_r = 9.75 \text{ \AA}$ , $\alpha'_r = 19.1^\circ$ .



FIGS. 3 and 4: FIG. 3 (left). Orientation of the Fe-O octahedral layer in relationship to the true cell and sub-cell  $x$  and  $y$  axes. FIG. 4 (right). Arrangement of rings of six tetrahedra in the unit cell. The figure shows the tetrahedra at only one  $z$ -level projected on to the (0001) plane.

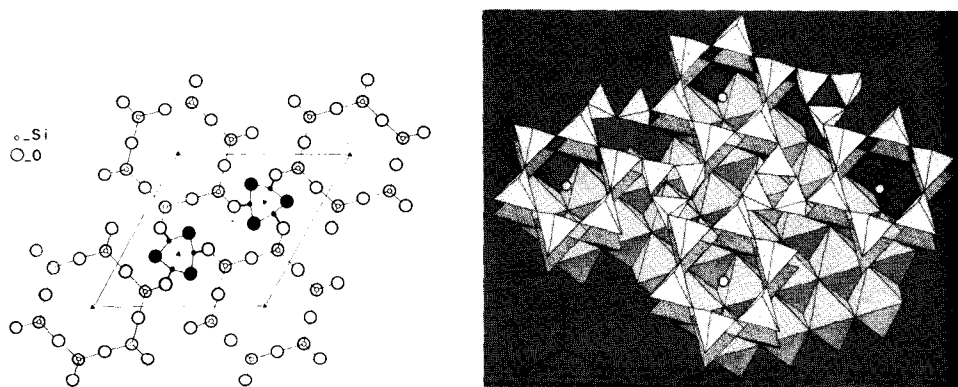
came directly over one another and were not staggered,<sup>1</sup> and that potassium atoms lay symmetrically placed between the rings; both of these arrangements are similar to those found for the micas. The structure at this stage had accounted for all atoms except six silicon and six oxygen atoms.

The feasibility of this trial structure was tested further by means of a one dimensional Fourier synthesis, using only  $00l$  reflections to give a projection of the electron density on to the  $c$  axis. The structure was represented quite well by this except that additional electron density seemed to be required with the same  $z$  coordinates as the potassium atoms. The surplus silicon and oxygen atoms were then placed to form three-membered rings of tetrahedra as shown in fig. 5, and the resulting structure

<sup>1</sup> Only if these rings of tetrahedra are directly opposed across the K atom do subsequent layers build up to give a sub-cell of Fe atoms which is rhombohedral as required.

(fig. 6) gave good agreement between observed and calculated  $F$  values ( $R = 0.16$ ). It was further noted that the number of octahedral corners not linked to tetrahedra was exactly that required to match the  $14(\text{OH})$  ions per layer given by the chemical formula. Alternative, structurally less plausible, arrangements gave less good agreement.

The intensity statistics for zussmanite were plotted after the manner of Howells *et al.* (1950) with the result shown in fig. 7. The  $N(z)$  curve is seen to lie well above that for a centrosymmetric structure, indicating, as would be expected for the structure



FIGS. 5 and 6: FIG. 5 (left). Arrangement of silicon and oxygen atoms (solid circles) forming rings of three tetrahedra which link the six-membered rings. (Projection on (0001).) FIG. 6 (right). Perspective view of the structure of zussmanite, showing one layer of Fe-O octahedra with the six-membered rings of downward-pointing tetrahedra linked to the upper side of it. Above these are six-membered rings of tetrahedra pointing upwards towards the next octahedral layer (not shown). Three-membered rings of tetrahedra and their linkage, and potassium atoms, are also shown. In the full structure, successive layers of octahedra are offset in the  $xy$  plane in accordance with rhombohedral stacking.

postulated, the presence of 'hypersymmetry' (Rogers and Wilson, 1953). The inference of centrosymmetry could not be taken as necessarily applying to the structure as a whole, since it could refer only to those parts of the structure that define the small pseudo-cell. A test for piezoelectricity was carried out by the method of Giebe and Scheibz, and the result was negative. There was thus no direct conclusive evidence that the space group of zussmanite is  $R\bar{3}$  and not  $R3$ ; the structure described is, however, centrosymmetric.

Refinement of the structure was carried out by the method of least squares, using form factors for the dominant ion in the various structure groups, i.e. K, Fe, Si, and O. The  $R$  value obtained was 16% using all possible reflections<sup>1</sup> and 12.5% if the unusually large number of unobserved reflections were omitted. Atomic coordinates and isotropic temperature factors are listed in table II.

Interatomic distances and bond angles are listed in tables III and IV, in which atoms are labelled in accordance with figs. 8, 9, 10, and 11.

<sup>1</sup> A complete list of  $F$  values is contained in the Ph.D. thesis by A. Lopes-Vieira, University of Oxford. A copy of the list may be obtained from J. Zussman.

TABLE II. Atomic coordinates referred to 'hexagonal cell', and isotropic temperature parameters. Standard deviations ( $\times 10^4$ ) are given in brackets

Atoms	Key nos. (figs. 8-11)	$x/a$	$y/a$	$z/c$	$U (\text{\AA})^2$
Fe,Mg	1	0	0	0	0.0126 (13)
Fe,Mg	2	0.2294 (3)	-0.0761 (3)	-0.0009 (1)	0.0068 (4)
Fe,Mg	3	0.3840 (3)	0.5387 (3)	-0.0035 (1)	0.0060 (4)
OH	11	1/3	2/3	0.0332 (8)	0.0141 (43)
OH	1, 2, 3, 4, 5, 6	0.1776 (16)	0.0510 (16)	0.0352 (5)	0.0167 (25)
O	8, 13	0.4111 (14)	-0.0253 (14)	0.0375 (4)	0.0103 (22)
O	7, 9, 12	0.2579 (14)	0.3598 (14)	0.0381 (4)	0.0108 (22)
OH	10, 14	0.4826 (14)	0.2813 (15)	0.0367 (4)	0.0124 (23)
Si	1	0.2570 (5)	0.3730 (5)	0.0932 (1)	0.0045 (7)
Si	2	0.4098 (5)	-0.0403 (5)	0.0935 (1)	0.0049 (7)
O	15	0.2661 (14)	-0.1567 (14)	0.1111 (4)	0.0127 (22)
O	18	0.4008 (14)	0.4893 (13)	0.1114 (4)	0.0099 (20)
O	17	0.2222 (13)	0.2368 (14)	0.1186 (4)	0.0118 (22)
O	16	0.4452 (14)	0.0951 (14)	0.1192 (4)	0.0130 (23)
O	19, 20	0.5300 (13)	0.3228 (13)	0.1664 (4)	0.0097 (18)
Si	3	0.5246 (5)	0.1797 (5)	0.1670 (2)	0.0051 (7)
K	—	1/3	2/3	1/6	0.0149 (18)

### Discussion

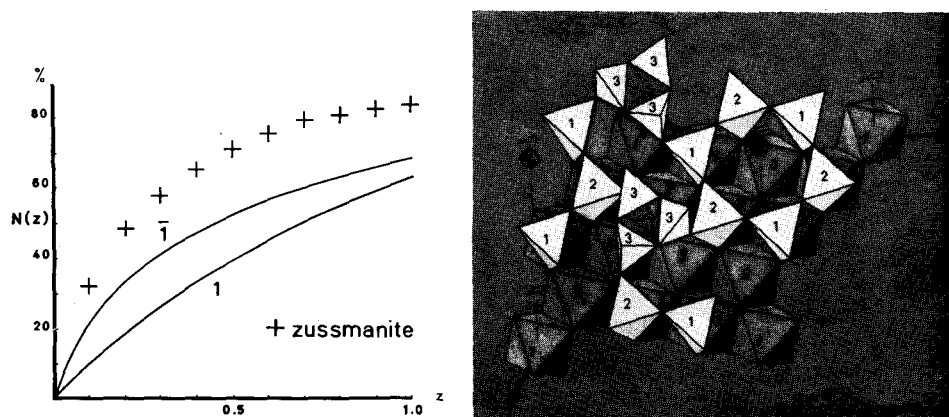
The mineral zussmanite should clearly be classed as a layered silicate since its structural units are ideally of infinite lateral extent but of discrete thickness. Its structure has close affinities to that of the trioctahedral micas in having a layer of Fe-O octahedra sandwiched between inward pointing tetrahedra. The latter, however, instead of forming continuous sheets of six-membered rings, are grouped in separate rings of six and these are linked by sharing corners with rings of three tetrahedra. The gaps between successive sandwiches are filled partly by potassium atoms (occurring only between pairs of six-membered rings and so fewer than in mica), and partly by the rings of three tetrahedra. The tetrahedral component has some degree of three-dimensionality since some of its tetrahedra share all corners. Its Si:O ratio is 9:21 and its sharing coefficient is 1.83 as compared with 2.5 and 1.75 for micas and 1.2 and 2.0 for framework silicates (Zoltai, 1960).

*Rings of three tetrahedra* of the kind found in zussmanite have been reported also for benitoite ( $\text{BaTiSi}_3\text{O}_9$ ; Zachariassen, 1930), wadeite ( $\text{Zr}_2\text{K}_4\text{Si}_6\text{O}_{10}$ ; Henshaw, 1956), pseudowollastonite ( $\text{CaSiO}_3$ ; Dornberger-Schiff, 1961), and margarosanite ( $\text{Pb}[\text{Ca},\text{Mn}]_2\text{Si}_3\text{O}_9$ ; Freed, 1969). Interatomic distances and angles within these rings are broadly similar for all five structures. For zussmanite, the  $\text{Si}_3\text{-O-Si}_3$  bridge angle of approximately  $132^\circ$  is somewhat smaller than others in the structure. O-Si-O angles are close to ideal in these rings, but Si-O distances are a little larger than usual (average 1.65 Å).

*Rings of six tetrahedra.* Although only trigonal and not hexagonal symmetry is imposed upon the rings of six tetrahedra, they are nevertheless remarkably close to being hexagonal. The four independent Si-O distances for the ...Si-O-Si... ring are

3.08, 3.07, 3.05, 3.06 Å, the two Si–O–Si angles are 142.5 and 142.0°, and the two O–O–O angles are 120.4 and 119.6° (107.24 and 132.8° in ferri-annite; Donnay *et al.*, 1964a). These rings are thus more nearly hexagonal than corresponding rings in many micas, and this fact is reflected also in the potassium–oxygen coordination polyhedron with K–O distances 3.00 and 3.01 Å as compared with 3.05 and 3.35 Å in ferri-annite.

In zussmanite the adjustment of the six-membered rings of tetrahedra to the rather larger dimensions of the octahedral layer is achieved by a regular tilting outwards of



FIGS. 7 and 8: FIG. 7 (left). Test for centro-symmetry (after Howells *et al.*, 1950). The curve obtained for zussmanite is consistent with the presence of hyper-symmetry. FIG. 8 (right). Perspective view of part of zussmanite structure with tetrahedra and octahedra labelled for tabulating interatomic distances and angles.

all tetrahedra rather than by the rotations and tilts observed in many micas. This is possible because the six-rings are not linked directly to one another. The outward tilt of the tetrahedron also allows the linkage between opposite 6-rings by means of an edge of a tetrahedron in the ring of three. The potassium coordination polyhedron (fig. 11) shows the distance between opposing inner basal oxygens to be 3.18 Å, whereas the outer basal oxygens are separated by 2.74 Å (the tetrahedral edge  $O_{16}-O_{17}$ ). The degree of tilting is also indicated by the difference in  $z$ -coordinates (0.23 Å) as between atoms ( $O_{16}, O_{17}$ ) and ( $O_{15}, O_{18}$ ) making the basal oxygens of the tetrahedra non-coplanar. Because of the constraint of the ring of three tetrahedra the 'inter-layer' distance 3.18 Å is small compared with the corresponding 3.40 Å in ferri-annite.

*Octahedral layer.* It is of interest to compare the octahedral layer in zussmanite with that in certain trioctahedral micas. In all of these minerals the octahedra are not regular but are flattened in the direction perpendicular to the layer. The flattening is shown clearly by comparison of shared and unshared edges as in table V, and it can be seen to be most pronounced in zussmanite. The similarity in octahedral dimensions is closest between zussmanite and ferri-annite, as would be expected since the latter has an octahedral layer fully occupied by Fe ions. The flattening has been interpreted

TABLE III. *Interatomic distances*

Fe-O and Fe-OH distances in octahedral layer (in Å ± 0.02). First number refers to iron; second number refers to (O,OH). (OH) ions are 1, 2, 3, 4, 5, 6, 10, 11, 14

Octahedron 1		Octahedron 2		Octahedron 3	
I-1	2.11	2-2	2.13	3-8	2.21
I-2	2.11	2-6	2.10	3-10	2.11
I-3	2.11	2-7	2.19	3-11	2.14
I-4	2.11	2-8	2.19	3-12	2.21
I-5	2.11	2-9	2.15	3-13	2.11
I-6	2.11	2-10	2.11	3-14	2.12
Average	2.11	Average	2.14	Average	2.17

(O,OH)-(O,OH) distances in octahedral layer (in Å ± 0.03).

Octahedron 1 (OH)<sub>1</sub>-(OH)<sub>2</sub> and five equivalents: 3.20 (long edges)

(OH)<sub>1</sub>-(OH)<sub>6</sub> and five equivalents: 2.74 (short edges)

Octahedron 2				Octahedron 3			
7-8	3.25	7-10	2.84	11-12	3.23	11-14	2.77
8-2	3.26	10-8	2.81	12-8	3.21	14-12	2.84
2-7	3.25	8-9	2.85	8-11	3.24	12-13	2.85
9-6	3.24	9-2	2.83	13-10	3.22	13-8	2.84
6-10	3.21	2-6	2.74	10-14	3.32	8-10	2.81
10-9	3.18	6-7	2.83	14-13	3.24	10-11	2.77
Average (long)	3.23	Average (short)	2.82	Average (long)	3.24	Average (short)	2.81

Distances in tetrahedral layer (Å ± 0.02)

Si-Si distances

I-2	3.08	I-3	3.05	3-3	2.99
I'-2	3.07	2-3	3.06		

Si-O distances (Si numbers given first)

Tetrahedron 1		Tetrahedron 2		Tetrahedron 3	
I-7	1.59	2-8	1.62	3-16	1.67
I-15	1.63	2-15	1.62	3-17	1.67
I-17	1.60	2-16	1.60	3-19	1.64
I-18	1.63	2-18	1.62	3-20	1.64
Average	1.61	Average	1.61	Average	1.65

O-O distances

Tetrahedron 1		Tetrahedron 2		Tetrahedron 3	
7-15	2.68	8-15	2.66	16-17	2.74
7-17	2.64	8-16	2.66	16-19	2.71
7-18	2.64	8-18	2.69	16-20	2.69
15-17	2.64	15-16	2.63	17-19	2.69
15-18	2.55	15-18	2.63	17-20	2.73
17-18	2.63	16-18	2.62	19-20	2.66
Average	2.63	Average	2.65	Average	2.70

K-(O,OH) distances (Å ± 0.02)

K-O (15)	3.00	K-O (18)	3.01	K-OH (11)	3.83
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O-O distances in K coordination polyhedron (Å ± 0.03)

11-15	3.39	11-18	3.40	15-18	3.18
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TABLE IV. *Interatomic angles*

O-Fe-O angles in octahedral layer ( $\pm 0.7^\circ$ ). Numbers refer to (O,OH) atoms					
Octahedron 1					
1-2	98.9	1-4	180	1-5	81.1
Octahedron 2					
2-6	80.7	6-7	82.5	7-9	178.2
2-7	97.7	6-8	179.8	7-10	82.5
2-8	98.1	6-9	99.2	8-9	82.4
2-9	83.1	6-10	99.4	8-10	81.7
2-10	179.8	7-8	95.9	9-10	96.7
Octahedron 3					
8-10	81.2	10-11	81.5	11-13	178.0
8-11	96.3	10-12	173.8	11-14	81.4
8-12	93.4	10-13	99.4	12-13	82.8
8-13	82.1	10-14	103.4	12-14	81.9
8-14	174.5	11-12	96.2	13-14	100.1
O-Si-O angles in tetrahedra ( $\pm 1^\circ$ )					
Tetrahedron 1					
7-15	112.9	7-18	110.3	15-18	108.9
7-17	111.5	15-17	109.8	17-18	103.1
		Average	109.4		
Tetrahedron 2					
8-15	110.4	8-18	112.5	15-18	103.7
8-16	111.6	15-16	109.4	16-18	108.9
		Average	109.4		
Tetrahedron 3					
16-17	110.3	16-20	108.7	17-20	109.0
16-19	109.5	17-19	111.1	19-20	108.3
		Average	109.5		
Si-O-Si bridge angles ( $\pm 0.7^\circ$ )					
1-15-2	142.5	1-18-2	142.0		
1-17-3	137.6	2-16-3	138.9		
3-19-3	131.6				
O-O-O angles in rings of six tetrahedra ( $\pm 0.8^\circ$ )					
18-15-18	120.4				
15-18-15	119.6				

as due to a tendency for shared oxygens to come closer and thereby shield neighbouring Fe atoms from one another.

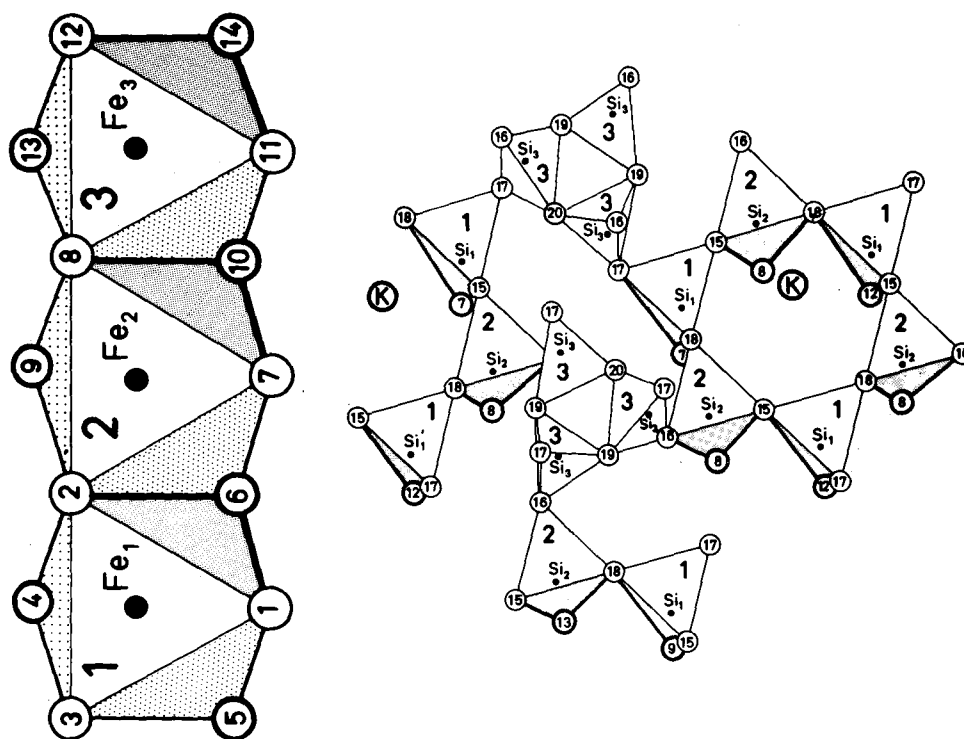
There are three non-equivalent Fe octahedra in the structure, and the environment of each is quite different. Fe(1) has a three-membered ring on each side of the layer at the level of the potassium cations; these three-rings are not linked directly to the octahedral layer. The Fe(2) octahedron shares oxygens with three tetrahedra, two on one side of the octahedral layer and one on the other. The Fe(3) octahedron similarly shares oxygens with three tetrahedra but in addition it has a potassium atom on one



TABLE V. Lengths of shared and unshared edges of octahedra in phlogopite, ferri-annite, ferri-phlogopite, and zussmanite

	Shared	Unshared	Zussmanite	Shared	Unshared
Phlogopite*	2.80 Å	3.05 Å	Average of all octahedra	2.79	3.22
Ferri-annite†	2.81	3.14	Average of octahedron 1	2.74	3.20
Ferri-phlogopite†	2.85	3.10	Average of octahedron 2	2.82	3.23
			Average of octahedron 3	2.81	3.24

\* Zvyagin and Mishchenko, 1962.

† Donnay *et al.*, 1964a.

FIGS. 9 and 10: FIG. 9 (left). Part of octahedral layer showing three crystallographically distinct octahedra with oxygens labelled for tabulating interatomic distances and angles. Oxygens that are not shown are related by symmetry to others that are. FIG. 10 (right). Rings of six and three tetrahedra with Si and O atoms labelled.

side and a three-ring at the same distance on the other. The Fe(3) octahedron is displaced slightly from the plane of the octahedral layer away from the potassium; the octahedral layer is thus not perfectly flat, but has slight hummocks in it alternating in direction since they are always concave toward the neighbouring potassiums.

Further differences are noted between the three kinds of Fe octahedron. In Fe(1), all Fe-O distances are equal and relatively short, whereas in the Fe(3) octahedron,

because of the K ion on one side,  $\text{Fe}_3\text{-O}_8$  and  $\text{Fe}_3\text{-O}_{12}$  are significantly larger than the three distances on the other side of the octahedron ( $\text{Fe}_3\text{-O}_{11}$  is also slightly longer). In the Fe(2) octahedron also, the two oxygens nearest to the K ion ( $\text{O}_7$  and  $\text{O}_8$ ) are furthest from Fe(2). The relationship between the K ions and distortions of the

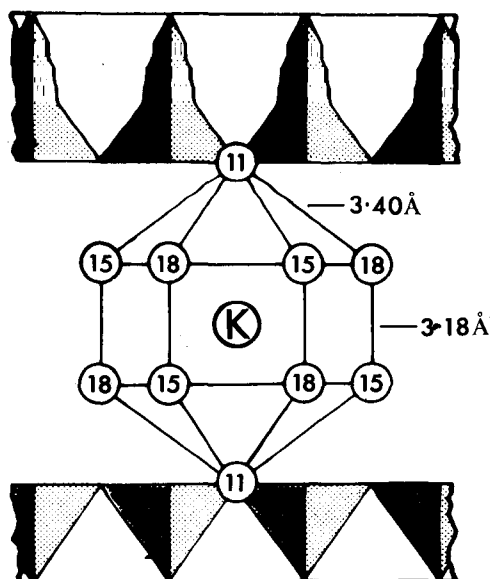


FIG. 11. Co-ordination polyhedron of oxygens around a potassium atom (approximately a hexagonal prism and bipyramid).

TABLE VI

Anions	Cations			Sum of valence strengths
	Fe = $\frac{1}{3}$	K = $\frac{1}{12}$	Si = 1	
(OH) <sub>11</sub>	$3 \times \frac{1}{3} \times 2$	—	—	1
(OH) <sub>1</sub>	$3 \times \frac{1}{3} \times 2$	—	—	1
(OH) <sub>10</sub>	$3 \times \frac{1}{3} \times 2$	—	—	1
O <sub>8</sub>	$3 \times \frac{1}{3} \times 2$	—	$1 \times \frac{1}{4} \times 4$	2
O <sub>7</sub>	$3 \times \frac{1}{3} \times 2$	—	$1 \times \frac{1}{4} \times 4$	2
O <sub>15</sub>	—	$1 \times \frac{1}{12} \times 1$	$2 \times \frac{1}{4} \times 4$	$2 \frac{1}{12}$
O <sub>18</sub>	—	$1 \times \frac{1}{12} \times 1$	$2 \times \frac{1}{4} \times 4$	$2 \frac{1}{12}$
O <sub>17</sub>	—	—	$2 \times \frac{1}{4} \times 4$	2
O <sub>16</sub>	—	—	$2 \times \frac{1}{4} \times 4$	2
O <sub>19</sub>	—	—	$2 \times \frac{1}{4} \times 4$	2

octahedral layer may contribute to the production in general of a regular layer stacking sequence.

*Layer stacking.* It was observed on the X-ray photographs that the strong pseudocell reflections were relatively sharp whereas the other reflections were weak and slightly streaked parallel to  $c^*$ . The degree of streakiness varies from one crystal to another.

In a regular rhombohedral stacking the layer sequence is *ABCABC*, etc., with displacements of  $(\frac{1}{3}, \frac{2}{3})$  between successive layers. The possibility of mistakes in layer stacking giving rise to other layer sequences was considered. If the strong reflections were considered as produced mainly by the Fe atoms, and displacements of the layers left the Fe arrangement undisturbed, this might have explained the observed effects. However, no reasonable system of displacement could be postulated which did not also involve changes in the Fe layer sequence, making these *AAA* or *ABAB* or random. Any of these sequences would have given an array of sub-cell reflections different from those observed.

A more likely explanation of the streaks is that there are displacements of the silicon-oxygen layers parallel to (0001), by translations corresponding to the  $x'$   $y'$  vectors of the small pseudo-cell, or multiples of these. The observed rule that only reflections with  $k = 3h \pm 13n$  would be sharp, would be obeyed.

It follows from the above that the structure is to a small degree disordered, and that the rhombohedral symmetry observed is strictly that of an 'average' structure. Also, agreement between observed intensities and those calculated for a regular structure would perhaps be a little better if there were no disorder in the structure.

The *valency balance* in zussmanite is shown in table VI, ignoring the small amount of trivalent ions replacing  $\text{Fe}^{2+}$  and assuming that no Al is present replacing Si. It is seen that the unbalance on  $\text{O}_{15}$  and  $\text{O}_{18}$  would be cancelled if one in six of the silicon atoms of the six-membered rings were replaced by aluminium. This proportion of two per formula unit is a little higher than that given by the chemical analysis (1.4 per formula unit). Substitution of aluminium for a number of silicon atoms that is not a multiple of three is a further indication that the rhombohedral symmetry of the structure is statistically rather strictly obeyed. It is tempting to speculate whether a version of the zussmanite structure entirely lacking in both potassium and aluminium would be viable, and also whether a magnesium end-member could exist.

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