

## Redetermination of the crystal structure of clinohedrite, $\text{CaZnSiO}_4 \cdot \text{H}_2\text{O}$

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### Auszug

Die Kristallstruktur des Klinohedrits,  $\text{CaZnSiO}_4 \cdot \text{H}_2\text{O}$ , von Franklin, New Jersey, wurde mit Hilfe dreidimensionaler Diffraktometer-Daten (Philips PW 1100) neu bestimmt. Sie ist von derjenigen von NIKITIN and BELOV (1963) wesentlich verschieden. Die Gitterkonstanten, ermittelt nach der Methode der kleinsten Quadrate mit direkt auf dem Diffraktometer gemessenen  $\theta$ -Werten, sind:  $a = 5,090$ ,  $b = 15,829$ ,  $c = 5,386 \text{ \AA}$ ,  $\beta = 103,26^\circ$ ;  $Z = 4$ , Raumgruppe  $Cc$ . Atomparameter und anisotrope Temperaturfaktoren wurden nach der Methode der kleinsten Quadrate bis zu  $R = 0,041$  verfeinert.

Die Struktur enthält isolierte  $\text{SiO}_4$ -Tetraeder, nicht  $\text{Si}_2\text{O}_7$ -Gruppen. Das  $\text{SiO}_4$ -Tetraeder ist fast regelmäßig mit  $\langle \text{Si}-\text{O} \rangle = 1,620 \text{ \AA}$  und  $\langle \text{O}-\text{O} \rangle = 2,645 \text{ \AA}$ . Die Zn-Atome sind von vier O-Atomen in den Ecken eines verzerrten Tetraeders umgeben;  $\langle \text{Zn}-\text{O} \rangle = 1,959 \text{ \AA}$  und  $\langle \text{O}-\text{O} \rangle = 3,181 \text{ \AA}$ . Jedes Ca-Atom ist von vier O-Atomen und zwei  $\text{H}_2\text{O}$ -Molekülen umgeben, welche ein stark verzerrtes Oktaeder bilden;  $\langle \text{Ca}-\text{O} \rangle = 2,372 \text{ \AA}$  und  $\langle \text{O}-\text{O} \rangle = 3,306 \text{ \AA}$ .

Jedes  $\text{ZnO}_4$ -Tetraeder hat gemeinsame Ecken mit vier benachbarten  $\text{SiO}_4$ -Tetraedern, zwei anderen  $\text{ZnO}_4$ -Tetraedern und zwei  $\text{CaO}_6$ -Oktaedern, wobei zweidimensionale  $(\text{ZnSiO}_4)_n^{-2n}$ -Netze, parallel (010), zustande kommen. Das  $\text{CaO}_6$ -Oktaeder hat gemeinsame Ecken mit vier  $\text{SiO}_4$ - und zwei  $\text{ZnO}_4$ -Tetraedern. Außerdem hat es zwei Kanten mit benachbarten Oktaedern gemeinsam. Auf diese Weise werden unendliche Zickzack-Ketten gebildet, welche mit der Periode von zwei Oktaedern parallel (100) entlang der  $c$ -Achse verlaufen. Die benachbarten parallelen Oktaeder-Ketten werden durch  $\text{SiO}_4$ -Tetraeder verbunden und bilden unendliche Schichten senkrecht zu  $b$ . Jede Oktaeder-Schicht verbindet zwei  $(\text{ZnSiO}_4)_n^{-2n}$ -Schichten. Wird die Oktaeder-Schicht mit A und die  $(\text{ZnSiO}_4)_n^{-2n}$ -Schicht mit B bezeichnet, dann ist das Bauprinzip ...ABABA... entlang der  $b$ -Achse.

### Abstract

The crystal structure of clinohedrite,  $\text{CaZnSiO}_4 \cdot \text{H}_2\text{O}$ , has been redetermined, using three-dimensional intensities measured with an automated Philips PW 1100 single-crystal diffractometer. The structure differs substantially

from that of NIKITIN and BELOV (1963). The cell constants, obtained by least squares from direct  $\theta$ -value measurements on the diffractometer, are:  $a = 5.090$ ,  $b = 15.829$ ,  $c = 5.386$  Å,  $\beta = 103.26^\circ$ ;  $Z = 4$ . The space group is *Cc*. Atomic parameters and anisotropic temperature factors were refined by least squares to  $R = 0.041$ .

The structure contains isolated  $\text{SiO}_4$  tetrahedra and not  $\text{Si}_2\text{O}_7$  groups. The  $\text{SiO}_4$  tetrahedron is almost regular with an average Si—O distance of 1.620 Å and average O—O distance 2.645 Å. The Zn atoms are surrounded by four O atoms forming a distorted tetrahedron. The average Zn—O distance is 1.958 Å and the O—O distance 3.181 Å. Each Ca atom is octahedrally coordinated by four O atoms and two  $\text{H}_2\text{O}$  molecules. The Ca octahedron is highly distorted, with average Ca—O distance 2.372 Å and O—O distance 3.306 Å.

Each  $\text{ZnO}_4$  tetrahedron shares corners with four  $\text{SiO}_4$  tetrahedra, two other  $\text{ZnO}_4$  tetrahedra and two  $\text{CaO}_6$  octahedra. Two-dimensional network layers  $(\text{ZnSiO}_4)_n^{-2n}$ , parallel to (010), are formed. The  $\text{CaO}_6$  octahedron shares corners with four  $\text{SiO}_4$  and two  $\text{ZnO}_4$  tetrahedra; moreover, it shares two edges with two adjacent octahedra. In this way are formed infinite serrated zigzag chains parallel to (100) along the  $c$  axis, with a repeat period of two octahedra. Adjacent parallel chains in the [100] direction are linked together by  $\text{SiO}_4$  tetrahedra and thus form infinite layers perpendicular to  $b$ . Each layer of octahedra links two  $(\text{ZnSiO}_4)_n^{-2n}$  layers together. If the layer of octahedra is called A and the  $(\text{ZnSiO}_4)_n^{-2n}$  layer B, then the structural principle is ...ABABA... along the  $b$  axis.

### Introduction

Clinohedrite,  $\text{CaZn}[\text{SiO}_4] \cdot \text{H}_2\text{O}$  is a glassy, colorless or snow-white to amethystine mineral found at Franklin, New Jersey, U.S.A., in association with other calcium and zinc minerals, mostly hancockite, axinite, glaucochroite, willemite, hodgkinsonite and franklinite. It was first identified and described by PENFIELD and FOOTE (1898) and further studied in detail by PALACHE (1928, 1935). The crystals belong to the monoclinic domatic class and they are generally prismatic, tabular or wedge-shaped, with a perfect (010) cleavage. They are strongly pyroelectric.

Cell dimensions were first determined by STRUNZ (1941). Based upon approximate relationships between corresponding cell dimensions of clinohedrite and hemimorphite,  $\text{Zn}[(\text{OH})_2|\text{Si}_2\text{O}_7] \cdot \text{H}_2\text{O}$ , he cautiously suggested a similarity of the two structures. An approximate but entirely different structure was proposed by NIKITIN and BELOV (1963), in which the  $\text{SiO}_4$  tetrahedra were isolated, instead of forming  $\text{Si}_2\text{O}_7$  groups. Although the general features of the structure seemed to be rather correct, yet there were several serious discrepancies in the published paper and the results could only be accepted with caution (WYCKOFF, 1968). STRUNZ (1966, 1970) did not include the new

structure in subsequent editions of the *Mineralogische Tabellen*, but he continued classifying clinohedrite together with hemimorphite.

In view of the above situation and because of a long-range interest in the crystal-chemistry of various bivalent cations in silicates, a thorough and unambiguous structure determination of clinohedrite was considered worthwhile.

### Experimental

A few small clinohedrite crystals from sample No. 10520 of the Harvard Collection, were kindly given to one of us (P.J.R.) in 1963, by Professor C. FRONDEL, Harvard University. One of them was singled out and shaped into a small sphere 0.4 mm in diameter.

After centering the sphere on our computer-controlled PHILIPS PW 1100 four-circle single-crystal diffractometer, approximate cell dimensions were determined by using the peak-hunting routine of the instrument. More precise values were obtained in the following way: The  $\theta$  angles of 138 strong reflections were directly measured on the diffractometer and subsequently used in the least-squares program PARAM (part of the *X-ray system of crystallographic programs*; see STEWART *et al.*, 1972) for further treatment. The final values obtained are given in Table 1, together with those of STRUNZ (1941) and NIKITIN and BELOV (1963), in the orientation of the latter.

Systematic absences indicated two possible space groups: *Cc* and *C2/c*. The strong pyroelectricity of the crystals and the results of the

Table 1. *Unit cell data for clinohedrite*  
(Standard errors, given in parentheses, refer to the last digit)

	VENETOPOULOS and RENTZEPERIS (this paper)	STRUNZ (reoriented) (1941)	NIKITIN and BELOV (1963)
<i>a</i>	5.090(2) Å	5.24 Å	5.16 Å
<i>b</i>	15.829(6)	15.94	15.94
<i>c</i>	5.386(2)	5.43	5.41
$\beta$	103.26(3)°	103.93°	103.90°
<i>V</i>	422.38 Å <sup>3</sup>	440.26 Å <sup>3</sup>	431.94 Å <sup>3</sup>
<i>Z</i>	4	4	4

$\rho_{\text{meas}} = 3.28$  to  $3.33$  g · cm<sup>-3</sup> (C. PALACHE, 1935).

$\rho_{\text{calc}} = 3.414$  g · cm<sup>-3</sup>.

Space group: *Cc*.

intensity statistics favoured the non-centrosymmetric space group  $Cc$ , the same as in the structure of NIKITIN and BELOV (1963).

Three-dimensional intensity data were collected on the PW 1100 diffractometer in the  $\omega$ -scan mode, using  $\text{MoK}\alpha$  radiation, monochromated with a graphite monochromator. The intensities of 5560 reflections in the range  $\theta = 8\text{--}40^\circ$  of the reciprocal lattice were measured and subsequently averaged to 1294 non-equivalent reflections. Integrated intensities, corrected for absorption, were converted to  $|F_o|$  values in the usual way. For all subsequent computations the programs of the *X-ray System of crystallographic programs* (STEWART *et al.*) were used throughout.

### Determination of the structure and refinement

At first, the structure of NIKITIN and BELOV (1963), obtained with two-dimensional film data, was tested. In space group  $Cc$  there is only the equivalent position  $4a: x, y, z; x, \bar{y}, \frac{1}{2} + z; \frac{1}{2} + x, \frac{1}{2} + y, z; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$ , and so all the atoms must occupy this position. A structure factor calculation with the positional parameters, given in Table 2 of NIKITIN and BELOV's paper, resulted in an  $R$  value of 0.337. The fully ionized state for all atoms was assumed and probable isotropic temperature factors were assigned to them (no temperature factors are given in NIKITIN and BELOV's paper). Atomic scattering factors, and also anomalous dispersion corrections for Zn, Ca and Si, were obtained from the *International tables for x-ray crystallography* (1968). A single scale factor was used for the whole set of reflection data.

Table 2. Atomic parameters and equivalent isotropic temperature factors for clinohedrite, with standard deviations

Atom	$x$	$y$	$z$	$B$
Zn	0	0.24928(4)	0	0.22 $\text{\AA}^2$
Ca	0.3480(3)	0.5724(1)	0.6384(3)	0.22
Si	0.0139(4)	0.3618(1)	0.5183(4)	0.06
O(1)	0.1415(11)	0.9591(3)	0.8564(11)	0.70
O(2)	0.1876(9)	0.1443(3)	0.9489(9)	0.29
O(3)	0.1410(9)	0.2934(3)	0.3476(9)	0.39
O(4)	0.1279(10)	0.3406(3)	0.8155(9)	0.40
O(5)	0.1067(9)	0.5459(3)	0.9479(9)	0.32
H(1)	0.186	0.916	0.725	
H(2)	0.320	0.986	0.942	

Refinement of the structure by least squares, using the program CRYLSQ of the *X-ray System*, was attempted next. After several cycles  $R$  stopped at 0.331 and the structure would not refine any further. Calculation of the interatomic distances both with the original parameters and those of the last least-squares cycle, gave some unacceptable distances, *e.g.* Zn—O = 1.16 Å, Ca—O = 1.86 Å, Si—O > 1.82 Å, O—O = 0.81 Å. It was decided then to start the structure determination from the beginning.

First, the positions of the Zn and Ca atoms were found from a three-dimensional Patterson synthesis and then all the other non-hydrogen atoms were located by the heavy-atom method. Least-squares refinement with isotropic temperature factors and unit weights proceeded smoothly down to  $R = 0.046$ . Then anisotropic temperature factors were introduced and, in five further cycles, refinement of the atomic parameters practically converged at  $R = 0.041$ .

At this stage an attempt was made to locate the two H atoms of the water molecule in the asymmetric unit. However, in the presence of the heavy atoms no unambiguous positions could be found on the Fourier or the difference-Fourier maps. Consequently, their positions had to be inferred from the following considerations:

(a) The atom O(1) is the only oxygen atom not bonded to the Si atom. It is bonded only to two Ca atoms, whereas all the other atoms are linked to three cations (see Table 7). Consequently, it was very probable that the two H atoms would be attached to it.

Table 3. *Anisotropic temperature coefficients  $U_{ij}$  for clinohedrite with their standard deviations ( $\times 10^4$ )*

Temperature factor $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$						
Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Zn	28(2)	21(2)	33(2)	0	— 5(1)	0
Ca	28(3)	27(3)	26(3)	0	5(2)	0
Si	4(5)	10(5)	13(5)	0	5(4)	0
O(1)	67(17)	77(18)	112(18)	0	32(15)	0
O(2)	3(13)	48(15)	60(15)	0	4(11)	0
O(3)	40(15)	53(15)	45(15)	0	15(12)	0
O(4)	87(17)	45(15)	22(14)	0	—10(13)	0
O(5)	55(15)	24(15)	46(15)	0	35(12)	0
H(1)	84	84	84	0	19	0
H(2)	84	84	84	0	19	0





Table 4. (Continued)

h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>	h	k	l	F <sub>o</sub>	F <sub>c</sub>
7	9	-3	11.9	11.0	7	13	-6	17.3	16.4	7	17	-3	38.3	40.0	8	2	2	16.7	18.0	8	6	1	15.1	14.3	8	12	-3	23.4	24.5					
			-2	12.9	14.0			-5	45.7	47.9			-2	11.1	11.4	8	4	-6	16.6	14.9	8	8	-5	44.8	48.0			-2	9.7	10.0				
			-1	26.7	27.4			-4	17.5	18.9			-1	21.4	21.2			-5	20.1	21.1	8	8	-5	14.9	15.0			-1	21.1	20.3				
			0	15.5	14.8			-3	35.6	37.0			0	14.6	16.3			-4	18.3	18.3			-4	32.9	35.6			0	24.1	25.9				
			1	39.7	39.9			-2	30.1	29.8	8	0	-6	70.7	74.5			-3	23.6	24.6			-3	15.2	16.3	8	14	-2	40.8	44.2				
			2	12.2	13.8			-1	55.0	55.9			-4	47.8	49.7			-2	27.2	28.5			-2	57.2	58.7	9	1	-4	10.1	8.0				
			3	22.0	21.2			0	10.9	12.8			-2	16.7	16.6			-1	18.5	18.2			-1	20.3	18.5			-3	19.4	21.1				
7	11	-6	21.7	24.6				1	48.4	49.2			0	55.6	56.0			0	26.7	27.2			0	36.5	38.1			-2	22.0	22.7				
			-5	35.2	37.0			2	20.3	20.4			2	53.3	55.1			1	24.4	24.4			1	6.7	4.3			-1	29.1	31.5				
			-4	22.3	22.6	7	15	-5	34.5	36.1	8	2	-6	16.3	16.7			2	25.7	28.6	8	10	-5	28.9	30.7	9	3	-3	45.8	48.8				
			-3	39.8	40.6			-4	25.8	25.7			-5	8.7	9.9	8	6	-6	31.3	33.6			-4	37.7	40.4			-2	11.6	12.1				
			-2	22.5	20.6			-3	28.0	27.9			-4	29.3	30.4			-5	15.6	12.0			-3	15.4	16.7			-1	18.9	20.5				
			-1	45.2	46.0			-2	32.9	34.0			-3	31.2	31.0			-4	39.1	39.6			-2	35.4	34.5	9	5	-3	30.5	30.9				
			0	15.2	15.0			-1	36.7	39.2			-2	41.4	41.9			-3	9.8	8.3			-1	10.2	11.6			-2	16.3	16.3				
			1	19.3	19.4			0	14.2	14.4			-1	24.1	24.7			-2	13.0	12.1			0	36.9	37.7			1	24.0	24.5				
			2	10.6	12.2			1	45.8	48.1			0	36.7	36.9			-1	6.2	3.6			1	24.0	24.5									
			3	32.6	35.5	7	17	-4	5.3	8.4			1	21.2	23.1			0	35.2	37.2	8	12	-4	27.3	27.6									

(b) The known average dimensions and shape of the water molecule and also the probability that the bond directions around O(1) would be approximately tetrahedrally arranged, indicated probable positions for the two H atoms.

(c) The local charge balance in this arrangement is quite satisfactory and indicates hydrogen bonding systems with the oxygen atoms O(2) and O(5) (cf. Table 5).

The two H atoms, with probable isotropic temperature factors, were included in further least-squares refinement cycles with all their parameters fixed. A final  $R = 0.040$  was obtained.

The final atomic parameters are given in Table 2 and the anisotropic temperature coefficients  $U_{ij}$  in Table 3. Comparison between  $|F_o|$  and  $|F_c|$  values, obtained with the parameters in Tables 2 and 3, is made in Table 4. Interatomic distances and bond angles are given in Tables 5 and 6 and in Fig. 3. The coordination of the O atoms, with the corresponding distances and angles, is shown in Table 7.

### Description of the structure and discussion

Figure 1 shows the structure of clinohedrite projected along [100] on a perpendicular plane. The corresponding schematic representation of the structure, as formed by the coordination polyhedra around the cations, is shown in Fig. 2. The  $\text{SiO}_4$  tetrahedra do not form  $\text{Si}_2\text{O}_7$  groups but are isolated. The Zn atoms are tetrahedrally coordinated and the Ca atoms are bonded to six O atoms at the corners of a distorted octahedron. The O atom of the  $\text{H}_2\text{O}$  molecule belongs to the Ca octahedron only.



Table 5. *Interatomic distances in clinohedrite, with their standard deviations*

SiO <sub>4</sub> tetrahedron			
Si—O(2)	1.620 Å	O(2)—O(3)	2.678 Å
O(3)	1.645	O(4)	2.636
O(4)	1.608	O(5)	2.642
O(5)	1.608	O(3)—O(4)	2.644
Average Si—O	1.620 ± 0.005	O(5)	2.614
		O(4)—O(5)	2.657
		Average O—O	2.645 ± 0.007
ZnO <sub>4</sub> tetrahedron			
Zn—O'(2)	1.967 Å	O'(2)—O'(3)	2.883 Å
O'(3)	1.945	O''(3)	3.237
O''(3)	1.973	O'(4)	3.189
O'(3)	1.949	O'(3)—O''(3)	3.532
Average Zn—O	1.958 ± 0.005	O'(4)	3.297
		O''(3)—O'(4)	2.947
		Average O—O	3.181 ± 0.006
CaO <sub>6</sub> octahedron			
Ca—O(1)	2.414 Å	O(1)—O'(1)	2.987 Å
O'(1)	2.454	O''(2)	3.546
O''(2)	2.398	O'(4)	3.184
O'(4)	2.298	O(5)	3.187
O(5)	2.343	O'(1)—O''(2)	2.973
O'(5)	2.324	O(5)	3.084
Average Ca—O	2.372 ± 0.005	O'(5)	3.187
		O''(2)—O'(4)	3.918
		O'(5)	3.340
		O'(4)—O(5)	3.334
		O'(5)	3.874
		O(5)—O'(5)	3.060
		Average O—O	3.306 ± 0.007
H bonding			
O(1)—H(1)···O(2)	1.04—1.77 Å	O(1)—O(2)	2.791 Å
angle:	165°		
O(1)—H(2)···O(5)	1.01—1.73 Å	O(1)—O(5)	2.683 Å
angle:	154°		

Table 6. Bond angles in clinohedrite, with their standard deviations

SiO <sub>4</sub> tetrahedron		CaO octahedron	
O(2)—Si—O(3)	110.25°	O(1) —Ca—O'(1)	75.71°
	O(4) 109.51		O''(2) 94.92
	O(5) 109.90		O'(4) 84.98
O(3)—Si—O(4)	108.75		O(5) 84.09
	O(5) 106.96	O'(1) —Ca—O''(2)	75.56
O(4)—Si—O(5)	111.43		O(5) 79.96
			O'(5) 83.62
Average O—Si—O	109.47 ± 0.25	O''(2)—Ca—O'(4)	113.08
			O'(5) 90.02
		O'(4) —Ca—O(5)	91.82
			O'(5) 113.87
		O(5) —Ca—O'(5)	81.93
		Average O—Ca—O	89.13 ± 0.18
ZnO <sub>4</sub> tetrahedron			
O(2) —Zn—O'(3)	110.46°		
	O''(3) 94.95		
	O'(4) 109.03		
	O'(4)		
O'(3) —Zn—O''(3)	128.74		
	O'(4) 97.49		
O''(3)—Zn—O'(4)	115.72		
Average O—Zn—O	109.40 ± 0.19		

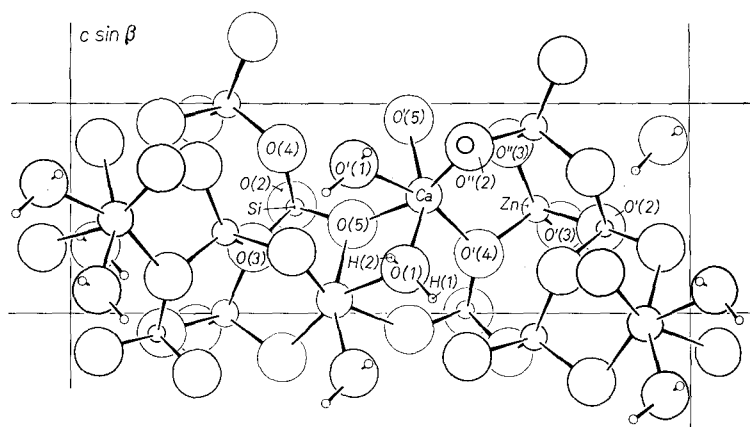


Fig. 1. Projection of the structure of clinohedrite along [100] on a perpendicular plane. The atoms of the asymmetric unit are labeled. The primed atoms are the symmetry-equivalent atoms shown in Fig. 3

In Fig. 3 are shown the coordination polyhedra around the cations, with the corresponding interatomic distances and angles (cf. Table 5). Their main characteristics are as follows:

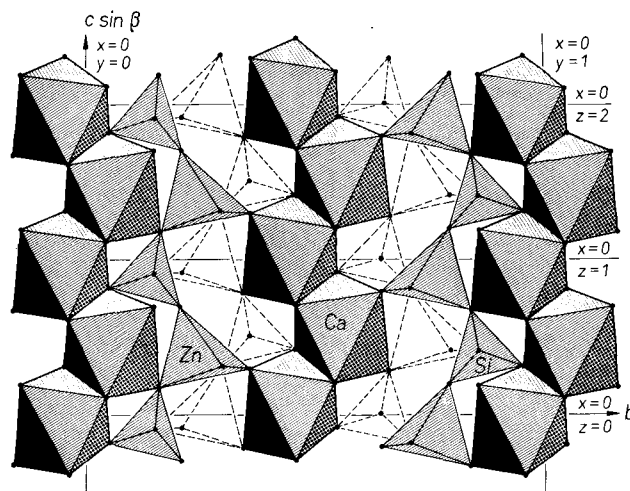


Fig. 2. Schematic representation of the structure, corresponding to Fig. 1, as formed by the coordination polyhedra around the cations. The edge-sharing Ca octahedral chains at  $y = 0$  and  $y = 0.5$  are at heights  $x = 0.848$  and  $x = 0.348$  respectively. Two unit cells are shown

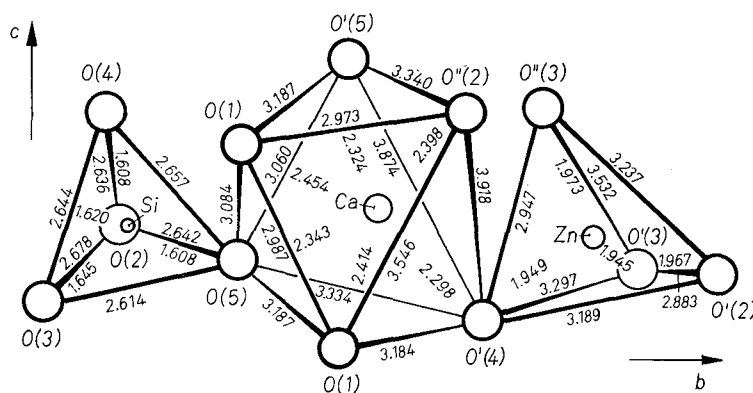


Fig. 3. Coordination polyhedra around the cations, shown separated from one another. The orientation of the polyhedra is for the cations in Fig. 1. Differences in height are indicated by heavier circles

### SiO<sub>4</sub> tetrahedron

The SiO<sub>4</sub> tetrahedron is almost regular with two shorter and one longer Si—O distances than the average, 1.620 Å. All the corners are shared by two other cations and in the case of O(2) and O(5) also by

Table 7. *Coordination of the O atoms with the corresponding distances and angles*  
(Standard errors are given in Tables 5 and 6)

O(1)—Ca	2.414 Å	Ca—O(1)—Ca'	93.18°
Ca'	2.454	H(1)	123.5
H(1)	1.04	H(2)	114.8
H(2)	1.01	Ca'—O(1)—H(1)	110.9
		H(2)	107.2
		H(1)—O(1)—H(2)	105.8
O(2)—Zn	1.967 Å	Zn—O(2)—Ca	101.72°
Ca	2.398	Si	121.49
Si	1.620	H(1)	104.0
H(1)	1.77	Ca—O(2)—Si	132.05
		H(1)	100.9
		Si—O(2)—H(1)	88.7
O(3)—Zn	1.973 Å	Zn—O(3)—Zn'	112.29°
Zn'	1.945	Si	131.25
Si	1.645	Zn'—O(3)—Si	116.38
O(4)—Zn	1.949 Å	Zn—O(4)—Ca	102.73°
Ca	2.298	Si	125.15
Si	1.608	Ca—O(4)—Si	129.11
O(5)—Ca	2.343 Å	Ca—O(5)—Ca'	98.52°
Ca'	2.324	Si	140.93
Si	1.608	H(2)	85.7
H(2)	1.73	Ca'—O(5)—Si	103.71
		H(2)	131.8
		Si—O(5)—H(2)	102.1

a H atom, forming part of a hydrogen-bonding bridge (cf. Table 7). The longest bond distance, 1.645 Å, corresponding to O(3), can be attributed to the fact that O(3) is linked to two symmetry-equivalent Zn atoms in tetrahedral coordination. The distances to O atoms, belonging to either two Ca octahedra or to one Ca octahedron and one Zn tetrahedron, are considerably shorter (1.620 and 1.608 Å). Four O—O distances do not differ much from the average value, 2.645 Å. Of the remaining two O—O distances, one is shorter than the average by 0.03 Å, and the other longer by an almost equal amount. The O—Si—O angles do not differ from the ideal value, 109.47°, by more than 2°.

The  $\text{SiO}_4$  tetrahedron is remarkably similar to the one found in hodgkinsonite,  $\text{Zn}_2\text{Mn}[(\text{OH})_2|\text{SiO}_4]$  (RENTZEPERIS, 1963), and in euclase,  $\text{AlBe}[(\text{OH})|\text{SiO}_4]$  (MROSE and APPLEMAN, 1962).

#### $\text{ZnO}_4$ tetrahedron

The Zn atom is surrounded by two O atoms without attached H atoms and two O atoms taking part in hydrogen bonding. The Zn—O bond distances form two pairs of almost equal distances, one shorter and one longer than the average value, 1.958 Å. This almost coincides with the value 1.954 Å found in hemimorphite (MCDONALD and CRUICKSHANK 1967) and the value 1.95 Å found in larsenite (PREWITT, KIRCHNER and PREISINGER, 1967), but it is a little shorter than the corresponding values in zincite, ZnO (SWANSON and FUYAT, 1953), willemite,  $\text{Zn}_2\text{SiO}_4$  (CHIN'HANG, SIMONOV and BELOV, 1970) and in hodgkinsonite (RENTZEPERIS, 1963), *i.e.* 1.973 Å, 1.97 Å and 1.972 Å respectively. The average O—O distance, 3.181 Å, is very close to the corresponding value 3.189 Å in hemimorphite, 3.213 Å in hodgkinsonite and 3.22 Å in willemite. The average O—Zn—O angle is close to the ideal value, yet some angles deviate considerably. The  $\text{ZnO}_4$  tetrahedron is more strongly distorted than in either hemimorphite or hodgkinsonite.

#### $\text{CaO}_6$ octahedron

The Ca atom is bonded to one O atom, without attached H atoms, three O atoms participating in hydrogen bonding and two O atoms of  $\text{H}_2\text{O}$  molecules. The octahedron is highly distorted. Three Ca—O distances are shorter and three longer than the average value 2.372 Å, which agrees well with the values found in other calcium silicates. For example, in bustamite,  $\text{CaMnSi}_2\text{O}_6$  (PEACOR and BUERGER, 1962), these values are 2.384 Å and 2.392 Å. It is of interest to note that the two longest distances are to the O atoms of the water molecules, which are tetrahedrally coordinated to four cations, and not to three or quasi four, as is the case with the other O atoms. The shortest distance is, as expected, to the O atom without attached H atoms, O(4). The average O—O distance, 3.306 Å, is quite similar to the corresponding distance in the  $\text{ZnO}_4$  tetrahedron, but in this case two distances are much larger. Most of the O—Ca—O angles differ considerably from 90°.

In terms of the coordination polyhedra the structure can be described as follows (Fig. 2 and Table 7): The  $\text{SiO}_4$  tetrahedra, while isolated from one another, share each of their corners with either two  $\text{ZnO}_4$  tetrahedra, O(3), or one  $\text{ZnO}_4$  tetrahedron and one  $\text{CaO}_6$  octahedron, O(2) and O(4), or two  $\text{CaO}_6$  octahedra, O(5). Each  $\text{ZnO}_4$  tetrahedron shares corners with four  $\text{SiO}_4$  tetrahedra, two other  $\text{ZnO}_4$  tetrahedra and two  $\text{CaO}_6$  octahedra. The  $\text{CaO}_6$  octahedron shares corners with four  $\text{SiO}_4$  and two  $\text{ZnO}_4$  tetrahedra; moreover, it shares two edges with two adjacent  $\text{CaO}_6$  octahedra. No polyhedron shares a face with another.

As a result of this arrangement, the  $\text{ZnO}_4$  and  $\text{SiO}_4$  tetrahedra form a network  $(\text{ZnSiO}_4)_n^{-2n}$ , extending in the (010) plane. In this network, the corner-sharing  $\text{ZnO}_4$  tetrahedra form infinite zigzag chains along the diagonal  $\mathbf{d} = \mathbf{a} - \mathbf{c}$  in the (010) plane. All the Zn atoms of a particular chain lie at a distance from the  $\mathbf{a}, \mathbf{c}$  plane of either  $b/4$  or  $3b/4$ .

In an analogous way, the edge-sharing  $\text{CaO}_6$  octahedra form infinite serrated zigzag chains, parallel to (100) along the  $c$  axis, with a repeat period of two octahedra. All the Ca atoms within a particular chain lie at either  $y = 0.348$  or  $0.848$ . Adjacent parallel chains in the [100] direction, separated by a distance equal to  $4.954 \text{ \AA}$  ( $a \sin \beta$ ), are linked together by  $\text{SiO}_4$  tetrahedra and form infinite two-dimensional layers of parallel chains of octahedra, perpendicular to the  $b$  axis at  $y = 0$  or  $y = 1/2$ . Due to the presence of the  $n$  glide plane in the unit cell, corresponding chains in neighboring layers along the  $b$  axis are translated by  $(\mathbf{a} + \mathbf{c})/2$ .

Each layer of octahedra links two  $(\text{ZnSiO}_4)_n^{-2n}$  network layers together. If we call A the layer of the parallel chains of  $\text{CaO}_6$  octahedra and B the network layer  $(\text{ZnSiO}_4)_n^{-2n}$ , both of which are parallel to (010), then the structure can be described with the pattern ...ABABA... along the  $b$  axis. This pattern explains well the perfect (010) cleavage of clinohedrite. Due to the greater valence of Si, the lower coordination around Si and Zn, and the shorter cation-anion distances in the B network layer, the bonding forces in it are much stronger than in A. Thus, cleavage would preferably occur at the O atoms connecting the two layers leaving B complete. It would require the breaking of only four Ca—O bonds for each unit cell. The cleavage surface would be parallel to (010).

Comparison of the structure found in this study with that described by NIKITIN and BELOV (1963), brought out the fact that,

despite the incongruities of the latter, mentioned earlier in this paper, the two structures are similar in their general features, though differing in detail. Careful search to account for it revealed the fact that the  $y$  and  $z$  coordinates, or only the  $z$  coordinate of the atoms except Zn and Si, published in the paper of NIKITIN and BELOV, should have been taken with the opposite sign and in the case of O(3) as  $\frac{1}{2}-z$  (cf. Table 2 of this paper with Table 2 in the paper of NIKITIN and BELOV). The correct coordinates yielded immediately the interatomic distances reported by these authors. In view of the rather restricted number of their film data (240  $0kl$  and  $hk0$  reflections), the cation-anion distances have a much larger spread than those reported here (Table 5). They are (for comparison, our values are given in parentheses): Si—O = 1.61—1.67 Å (1.608—1.645 Å); Zn—O = 1.89—2.204 Å (1.945—1.973 Å); Ca—O = 2.30—2.57 Å (2.298—2.454 Å).

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### References

- CHIN'HANG, M. A. SIMONOV and N. V. BELOV (1970), Crystal structures of willemite  $Zn_2[SiO_4]$  and its germanium analog  $Zn_2[GeO_4]$ . *Kristallografiya* **15**, 457—460 [Russ.]; *Soviet Physics—Crystallography* **15**, 387—390.
- International tables for x-ray crystallography*, vol. 3 (1968). The Kynoch Press, Birmingham.
- W. S. McDONALD and D. W. J. CRUICKSHANK (1967), Refinement of the structure of hemimorphite. *Z. Kristallogr.* **124**, 180—191.
- M. E. MROSE and D. E. APPLEMAN (1962), The crystal structures and crystal chemistry of väyrynenite,  $(Mn, Fe)Be(PO_4)OH$ , and euclase,  $AlBe(SiO_4)(OH)$ . *Z. Kristallogr.* **117**, 16—36.
- A. V. NIKITIN and N. V. BELOV (1963), The crystal structure of clinohedrite  $Ca_2Zn_2(OH)_2Si_2O_7 \cdot H_2O$ . *Dokl. Acad. Nauk SSSR* **148**, 1386—1388.
- CH. PALACHE (1928), Mineralogical notes on Franklin and Sterling Hill, N.J. *Amer. Mineral.* **13**, 297—329 (Clinohedrite, pp. 300—304).
- CH. PALACHE (1935), The minerals of Franklin and Sterling Hill, Sussex Country, New Jersey. *U.S. Geol. Survey Prof. Paper* 180, pp. 106—108.
- D. R. PEACOR and M. J. BUEGER (1962), Determination and refinement of the crystal structure of bustamite,  $CaMnSi_2O_6$ . *Z. Kristallogr.* **117**, 331—343.

- S. L. PENFIELD and H. W. FOOTE (1898), On clinohedrite, a new mineral from Franklin, N.J. *Amer. J. Sci.* **5**, 289–293.
- C. T. PREWITT, E. KIRCHNER and A. PREISINGER (1967), The crystal structure of larsenite  $\text{PbZnSiO}_4$ . *Z. Kristallogr.* **124**, 115–130.
- P. J. RENTZEPERIS (1963), The crystal structure of hodgkinsonite,  $\text{Zn}_2\text{Mn}[(\text{OH})_2|\text{SiO}_4]$ . *Z. Kristallogr.* **119**, 117–138.
- J. STEWART, G. KRUGER, H. AMMON, C. DICKINSON and S. HALL (1972), The X-RAY SYSTEM of crystallographic programs for any computer. Technical Rep., 192, Computer Science Center, University of Maryland.
- H. STRUNZ, *Mineralogische Tabellen* 1. Aufl. (1941), S. 182; 4. Aufl. (1966), S. 349; 5. Aufl. (1970), S. 392. Akademische Verlagsgesellschaft, Leipzig.
- H. E. SWANSON and R. K. FUYAT (1953), Standard x-ray diffraction powder patterns. National Bureau of Standards circular 539, vol. II, 62–63.
- R. W. G. WYCKOFF (1968), *Crystal structures*, 2nd edn., vol. 4, p. 260.