

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 θ -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 SiO_4 -Tetraeder, nicht Si_2O_7 -Gruppen. Das 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 H_2O -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 ZnO_4 -Tetraeder hat gemeinsame Ecken mit vier benachbarten SiO_4 -Tetraedern, zwei anderen ZnO_4 -Tetraedern und zwei CaO_6 -Oktaedern, wobei zweidimensionale $(\text{ZnSiO}_4)_n^{-2n}$ -Netze, parallel (010), zustande kommen. Das CaO_6 -Oktaeder hat gemeinsame Ecken mit vier SiO_4 - und zwei 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 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 θ -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 SiO_4 tetrahedra and not Si_2O_7 groups. The 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 H_2O molecules. The Ca octahedron is highly distorted, with average Ca—O distance 2.372 Å and O—O distance 3.306 Å.

Each ZnO_4 tetrahedron shares corners with four SiO_4 tetrahedra, two other ZnO_4 tetrahedra and two CaO_6 octahedra. Two-dimensional network layers $(\text{ZnSiO}_4)_n^{-2n}$, parallel to (010), are formed. The CaO_6 octahedron shares corners with four SiO_4 and two 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 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 SiO_4 tetrahedra were isolated, instead of forming Si_2O_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 θ 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
β	103.26(3)°	103.93°	103.90°
<i>V</i>	422.38 Å ³	440.26 Å ³	431.94 Å ³
<i>Z</i>	4	4	4

$\rho_{\text{meas}} = 3.28$ to 3.33 g · cm⁻³ (C. PALACHE, 1935).

$\rho_{\text{calc}} = 3.414$ g · cm⁻³.

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 ω -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 \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. Observed and calculated structure factors for clinohedrite

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c					
0	0	4	45.6	47.7	0	24	5	16.4	16.2	1	11	-1	100.5	103.5	1	25	0	20.4	20.6	2	10	-1	26.6	22.5	2	24	-1	15.9	16.1										
6	92.5	91.7	0	26	0	21.4	22.7	0	39.7	36.7	1	38.3	38.8	0	94.4	93.5	0	34.4	35.9																				
8	57.8	52.9	1	14.9	15.9	1	61.7	60.8	2	19.6	20.7	1	53.9	50.6	1	53.9	50.6	1	27.5	27.9																			
0	2	87.8	92.9	2	45.1	45.9	2	35.5	33.7	3	31.9	34.6	2	104.2	102.9	2	104.2	102.9	2	39.2	39.8																		
3	93.6	96.1	3	15.6	15.9	3	70.7	66.5	4	10.7	9.9	4	10.7	9.9	3	53.1	50.2	3	29.6	30.4																			
4	97.6	100.5	0	28	0	57.4	60.5	4	21.0	21.5	1	27	-3	25.0	27.6	4	74.6	73.1	4	26.4	24.5																		
5	33.8	32.6	1	15.6	13.7	5	70.6	70.5	-2	26.9	28.7	5	33.3	31.6	2	26	-3	33.3	31.6	2	26	-3	33.3	31.6	2	26	-3	33.3	31.6	2	26	-3	33.3	31.6	2	26	-3	33.3	31.6
6	53.6	53.0	1	1	-9	37.0	38.0	6	8.2	6.1	-1	25.5	27.5	6	54.9	55.3	-2	56.4	58.7																				
7	18.9	18.2	-8	10.5	10.7	7	35.5	37.5	0	16.0	18.0	7	12.1	13.1	7	12.1	13.1	-1	11.2	11.9																			
8	24.2	23.6	-7	17.4	19.6	8	10.0	10.5	1	16.1	17.0	8	36.4	37.6	0	47.1	49.6	0	47.1	49.6																			
9	11.4	11.5	-6	22.4	20.9	1	13	-8	21.4	18.7	2	12	-8	22.9	22.5	1	15.8	15.6	1	15.8	15.6																		
2	62.3	64.0	-5	28.9	30.1	-7	52.2	50.6	2	0	-8	37.8	34.6	-7	18.7	16.2	2	22.8	23.6																				
3	43.7	47.4	-4	40.2	49.7	-6	9.2	10.8	-6	83.6	81.6	-6	41.9	40.8	3	1	-9	30.5	31.6																				
4	43.7	42.1	-3	80.1	83.5	-5	77.1	76.5	-4	121.6	128.5	-5	20.3	18.4	-8	36.7	35.2																						
5	15.4	13.8	-2	81.5	85.5	-4	51.8	51.9	-2	35.6	36.3	-4	64.5	63.2	-7	47.2	47.2																						
6	30.6	30.9	2	39.3	35.9	-3	63.3	62.7	0	109.6	111.3	-3	29.6	27.7	-6	15.6	14.5																						
7	43.8	41.8	3	63.8	62.9	-2	22.5	19.3	2	178.5	210.1	-2	46.3	44.3	-5	29.9	28.6																						
8	32.2	30.1	4	48.3	45.7	-1	88.2	88.1	4	90.1	89.7	-1	53.2	50.4	-4	31.0	29.3																						
9	16.9	15.7	5	69.4	67.7	0	31.7	30.5	6	42.5	42.8	0	65.1	61.4	-3	40.2	37.8																						
0	6	1	50.9	47.9	6	36.8	34.9	1	117.1	118.4	8	58.6	59.2	1	40.8	37.2	-2	32.4	30.0																				
2	87.7	94.1	7	26.3	25.0	2	47.1	44.7	2	2	-9	30.5	29.8	2	54.8	51.7	-1	78.3	75.5																				
3	22.5	20.5	8	23.5	23.2	3	68.9	67.4	-8	51.0	50.6	3	15.4	11.1	0	79.9	75.9																						
4	32.6	28.8	9	16.0	15.4	4	12.4	9.1	1	18.4	18.4	4	60.9	40.5	5	37.3	36.2	2	47.3	44.3																			
5	8.5	8.3	1	3	-9	21.7	19.8	5	44.6	45.3	-5	28.3	27.2	6	22.9	20.3	3	17.1	16.5																				
6	51.0	49.0	-8	11.0	12.4	6	35.2	35.3	-4	73.8	73.2	7	29.4	29.5	4	11.1	9.7																						
7	26.1	25.0	-7	71.1	68.6	7	48.2	48.6	0	18.1	21.3	-3	33.7	36.0	2	14	-8	40.5	44.2																				
8	34.0	33.7	-6	44.5	42.1	8	18.1	21.3	8	18.1	21.3	2	14	-8	40.5	44.2	7	29.4	29.5																				
9	18.3	18.9	-5	87.2	88.2	1	15	-8	20.7	23.0	-2	113.7	123.4	-2	71.5	10.6	6	30.9	30.8																				
0	8	0	46.3	48.7	-4	56.9	55.5	-7	55.7	56.4	-1	86.2	84.2	-6	31.0	33.7	7	45.3	45.9																				
1	62.7	61.0	-3	64.7	67.1	-6	16.4	15.9	0	108.9	112.4	-5	12.4	7.9	8	22.5	23.1																						
2	110.5	119.7	-2	44.4	42.2	-5	62.5	60.8	1	67.2	62.9	-4	16.0	13.9	3	5	-9	82.3	88.1																				
3	40.5	39.1	2	44.5	39.6	-4	39.6	38.1	2	25.1	26.6	-3	7.8	8.2	7	8	-8	11.3	10.2																				
4	114.5	117.3	3	104.0	107.7	-3	56.8	53.2	3	22.4	22.1	-2	70.5	66.3	-2	27	-25.1																						
5	36.9	33.9	4	33.6	33.2	-2	46.7	44.9	4	54.8	53.4	-1	10.9	10.4	-6	9.0	5.7																						
6	50.1	50.3	5	35.9	34.1	-1	73.1	69.1	5	48.5	46.0	0	63.1	61.2	-5	83.5	82.7																						
7	8.3	8.8	6	28.6	27.2	0	25.7	26.4	6	63.5	62.4	1	22.6	21.9	-4	59.5	58.4																						
8	23.9	24.0	7	54.0	52.1	1	68.8	66.8	7	36.2	35.3	-2	9.4	8.5	-3	105.1	104.4																						
9	17.0	15.5	8	17.6	16.7	2	18.5	18.9	8	34.2	35.2	3	10.5	8.9	-2	43.3	40.9																						
0	10	0	133.3	151.3	9	49.0	51.4	3	55.3	55.1	2	4	-9	23.4	21.9	4	52.1	49.9	-1	76.9	74.1																		
1	67.8	66.8	1	5	-9	57.4	59.5	4	28.5	28.0	-8	29.5	32.5	5	8.5	9.5	0	23.2	21.5																				
2	104.1	107.1	-8	16.3	14.5	5	27.9	25.6	-7	20.7	20.1	6	44.9	45.1	1	82.9	79.9																						
3	26.9	25.6	-7	51.6	50.6	6	10.7	8.0	6	10.7	8.0	4	6	-6	40.3	38.0	5	58.6	55.8																				
4	71.6	71.7	-6	18.8	18.4	7	37.3	38.1	-5	59.6	58.1	2	16	-8	24.1	24.0	3	110.7	109.9																				
5	23.4	23.7	-5	74.1	70.7	1	17	-7	24.9	27.5	-4	40.5	40.1	-7	18.9	17.8	4	23.2	21.2																				
6	53.6	52.3	-4	27.7	26.6	-6	22.6	21.9	-3	15.9	14.9	-6	50.8	50.1	-5	72.3	71.4																						
7	30.3	29.4	-3	148.1	170.7	-5	16.4	11.2	-2	71.6	68.7	-5	11.1	10.8	6	16.7	16.3																						
8	30.8	30.6	-2	66.0	62.1	-4	22.0	22.0	-1	22.0	22.0	-1	22.0	22.0	-4	60.6	57.0																						
0	12	0	59.4	59.8	-1	135.8	149.8	-3	51.4	51.8	0	76.7	74.3	-3	52.1	50.8	8	8.0	6.9																				
1	28.8	28.9	1	20.5	19.8	-2	14.2	12.6	1	46.2	43.2	-2	59.2	57.7	3	5	-9	35.7	34.7																				
2	58.1	59.0	2	20.7	17.6	-1	63.1	62.8	2	55.6	52.6	-1	27.2	26.2	-8	19.2	19.2																						
3	60.6	59.0	3	93.5	95.2	0	22.3	20.4	3	50.0	46.0	0	64.1	61.5	-7	77.5	76.5																						

Table 4. (Continued)

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	
3 11	-8	10.0	9.8	3 25	2	16.6	16.8	4 12	-1	33.1	31.3	5 3	-1	90.4	86.9	5 17	1	42.2	43.8	6 10	3	16.1	15.6		
		-7 46.1	46.4	3 27	-1	19.1	19.7			0 42.7	40.3			0 10.3	8.3			2 15.5	13.2			4 37.4	39.4		
		-6 21.1	20.8	4 0	-8	50.0	49.8			1 39.8	38.1			1 50.3	46.9			3 33.3	33.9			6 12	-7	15.0	13.5
		-5 47.4	46.6	4 0	-6	31.4	30.9			2 48.8	47.2			2 27.6	26.8			4 16.2	15.0			-6	34.1	33.9	
		-4 15.8	14.0			-4 110.2	111.9			3 29.1	27.1			3 33.8	31.9	5 19	-6	17.8	18.8			-5	27.7	27.5	
		-3 58.2	56.0			-2 135.7	140.4			4 40.2	40.7			4 26.2	25.1			-5 14.8	14.2			-4	13.2	12.6	
		-2 36.3	35.5			0 36.0	33.2			5 10.9	8.5			5 60.7	61.0			-4 19.5	20.7			-3 33.4	32.4		
		-1 71.9	67.8			2 64.9	61.4			6 30.9	33.3			6 9.9	10.5			-3 34.3	32.5			-2 33.3	34.2		
		0 28.5	26.3			4 96.6	93.9	4 14	-8	24.6	24.1	5 5	-9	17.9	17.3			-2 16.2	16.2			-1 17.3	16.4		
		1 85.7	82.5			6 55.6	54.6			-7 13.8	12.5			-8 17.0	15.4			-1 44.5	44.9			0 45.4	44.5		
		2 29.8	27.2	4 2	-9	22.2	22.5			-6 38.5	39.3			-7 45.5	44.5			0 14.9	14.1			1 18.8	18.3		
		3 29.9	29.0			-5 10.1	7.0			-6 24.7	24.5			-6 24.7	24.5			1 27.3	28.2			2 32.8	32.4		
		4 31.6	31.1			-4 27.0	26.2			-5 88.2	87.3			-5 88.2	87.3			2 26.0	26.0			3 29.2	29.8		
		5 35.0	33.7			-3 7.9	8.8			-4 25.1	24.6			-4 25.1	24.6			3 32.8	33.2			4 32.3	32.7		
		6 15.7	16.3			-5 42.5	40.9			-2 14.1	12.6			-3 53.3	52.3	5 21	-5	26.9	30.4	6 14	-6	29.1	29.0		
		7 50.0	52.7			-3 64.1	62.4			-1 3.9	3.3			-2 21.0	18.9			-4 33.5	34.5			-5 9.6	8.3		
		-8 18.3	19.5			5 10.1	7.7			0 50.8	48.2			-1 52.5	49.5			-3 40.8	41.1			-4 44.7	45.6		
3 13	-7	29.1	27.9			5 40.0	38.0			1 13.9	14.9			0 14.5	13.4			-2 14.6	15.2			-3 6.7	2.5		
		-6 32.2	30.0			-1 42.1	39.2			2 50.7	49.2			1 103.7	101.0			-1 41.3	42.8			-2 17.8	15.9		
		-5 63.5	61.4			0 97.0	95.5			3 13.0	12.1			2 31.3	29.2			0 32.4	33.6			-1 10.9	10.4		
		-4 13.6	12.8			1 52.1	49.8			4 11.9	12.4			3 71.3	70.2			1 33.8	34.3			0 21.0	22.3		
		-3 87.9	85.4			2 80.8	78.2			5 4.3	4.2			4 20.5	20.3			2 15.1	17.6			1 4.9	5.8		
		-2 43.3	41.6			6 36.8	38.6	4 16	-7	24.4	24.7			5 36.9	38.5	5 23	-3	28.9	29.2			2 56.3	58.3		
		-1 64.2	61.3			4 31.0	29.8			-6 29.9	28.8	5 7	-8	9.2	8.3			-2 11.1	12.1			3 10.0	10.4		
		0 36.1	33.6			5 10.1	10.2			-5 36.5	36.8			-7 30.4	29.6			0 18.5	18.2	6 16	-6	34.2	34.4		
		1 79.5	77.8			7 27.5	27.5			-4 48.2	46.8			-6 8.7	5.3			1 44.9	48.4			-5 15.6	14.8		
		2 24.0	23.9			6 13.7	13.1			-3 17.7	16.4			-5 36.0	35.1			0 66.5	68.8			-4 31.3	30.9		
		3 88.8	85.9	4 4	-8	18.6	20.0			-2 57.1	55.1			-4 30.9	40.5	6 0	-8	66.5	68.8			-3 61.1	42.3		
		4 32.9	31.2			-7 28.8	27.4			-1 46.0	43.2			-3 45.8	44.4			-4 20.2	19.4			-2 37.9	38.4		
		5 49.4	49.4			-6 26.4	24.7			0 51.5	50.8			-2 50.0	47.2			-2 93.7	91.5			-1 22.1	21.3		
		6 15.3	14.7			-5 16.2	14.1			1 28.4	28.8			-1 44.8	43.7			9 98.9	97.7			0 47.3	47.3		
3 15	-8	21.1	20.8			2 27.3	25.7			2 38.1	37.4			2 43.1	42.5			2 13.9	13.9			1 21.4	17.9		
		-7 25.6	25.5			-3 66.8	64.6			3 25.4	26.2			1 36.6	35.1			4 35.6	35.6			2 34.3	33.9		
		-6 31.7	31.9			-2 24.5	23.1			4 44.7	46.0			2 18.8	17.6	6 2	-8	12.7	12.8			3 26.8	29.6		
		-5 56.9	57.5			-1 30.0	27.7			5 18.2	18.2			3 35.1	33.9			-7 16.6	16.9	6 18	-5	18.5	19.4		
		-4 6.4	5.5			0 44.2	40.6	4 18	-7	16.9	18.8			4 23.6	22.7			-6 36.3	33.6			-4 34.0	35.3		
		-3 74.7	72.4			1 35.1	32.2			-6 36.8	38.6			-5 37.7	36.2			-5 37.1	35.7			-5 25.7	25.3		
		-2 41.2	39.6			2 45.0	41.9			-5 26.8	27.4			6 35.4	34.6			-4 56.5	54.7			-2 45.9	48.1		
		-1 66.9	64.1			3 29.1	27.8			-4 59.6	61.9	5 9	-8	4.9	6.4			-3 39.4	38.7			-1 15.0	15.2		
		0 50.3	47.6			4 37.8	37.2			-3 15.7	15.7			-7 33.9	34.2			-2 56.7	53.9			0 56.6	59.0		
		1 62.9	59.8			5 29.5	28.3			-2 67.8	66.9			-6 27.0	25.7			-1 20.9	20.3			1 16.7	19.0		
		2 36.5	35.9			-1 25.3	25.6			-1 25.3	25.6			-5 14.8	14.8			0 40.8	38.9			2 43.7	43.7		
		3 62.0	61.6			7 28.1	27.8			0 56.4	54.4			-4 5.9	4.8			1 23.5	21.8	6 20	-4	40.4	43.1		
		4 9.6	10.2	4 6	-9	6.0	8.0			1 31.4	31.0			-3 44.9	43.5			2 58.1	57.4			-3 11.2	13.9		
		5 41.0	42.0			-8 27.0	28.7			2 43.0	42.0			-2 26.7	25.2			3 33.5	33.2			-2 36.9	38.2		
		6 17.9	17.9			-7 11.6	10.5			3 18.8	17.4			-1 62.3	59.7			4 53.2	54.5			-1 18.6	18.6		
3 17	-7	39.8	40.7			-6 1.1	9.7			-4 33.6	35.9			0 15.5	29.3			5 28.7	28.6			0 20.7	20.7		
		-6 6.8	4.2			-5 28.2	27.3			5 18.7	19.6			1 21.0	18.0	6 4	-8	20.5	21.5			1 22.1	23.1		
		-5 23.3	23.4			-4 58.4	55.7	4 20	-6	42.4	44.3			2 19.7	18.1			-7 18.2	17.8	7 1	-7	8.5	4.6		
		-4 25.6	22.9			-3 48.0	46.2			-5 21.9	22.1			3 37.6	38.1			-6 22.6	22.8			-6 7.1	7.0		
		-3 20.4	16.8			-2 73.2	70.3			-4 34.8	34.2			4 13.9	12.7			-5 33.0	32.4			-5 17.0	16.7		
		-2 19.9	18.9			-1 36.5	35.5			-3 22.4	22.5			5 30.7	30.0			-4 17.1	16.3			5 41.1	41.2		
		-1 47.1	46.2			0 46.6	43.3			-2 32.6	30.5			6 15.0	14.1			-3 11.3	9.4			-3 32.0	31.0		
		0 17.0	15.4			-1 15.9	12.9			-1 21.8	21.3	5 11	-8	18.4	19.6			-2 24.0	23.6			-2 33.9	33.5		
		1 46.8	45.5			2 42.2	40.7			0 45.5	45.5			-7 40.7	40.5			-1 47.3	44.6			-1 22.3	20.7		
		2 25.9	24.4			3 14.8	13.0			-6 16.6	16.9			-6 16.6	16.9			0 24.0	25.5			0 12.9	12.5		
		3 35.8	34.9			4 64.6	63.4			2 50.5	49.1			-5 14.9	14.7			1 31.1	30.7			1 14.4	13.7		
		4 14.5	14.5			5 18.5	18.9			3 13.1	12.3			-4 27.2	25.7			2 25.3	27.5			2 17.4	17.8		
		5 42.8	41.6			6 42.7	44.6			4 17.4	18.4			-3 57.4	56.3			3 20.6	20.2			3 38.4	39.7		
		6 8.1	5.2			7 14.1	15.9	4 22	-5	12.9	12.0			-2 12.8	10.6			4 21.5	21.0			4 18.8	19.8		
3 19	-7	17.0	17.9	4 8	-9	9.0	8.2			-4 27.1	28.3			-1 43.1	42.5			5 18.7	19.9	7 3	-7	54.7	57.1		
		-6 21.8	20.8			-8 43.0	43.4			-3 23.0	23.7			0 23.2	23.4	6 6	-8	40.4	41.9			-6 25.3	24.8		
		-5 40.0	37.2			-7 13.8	11.3			-2 42.5	42.9			1 55.0	52.7			-7 6.6	6.0			-5 54.4	54.6		
		-4 12.9	13.5			-6 83.5	84.0			-1 11.8	10.6			2 16.0	15.4			-6 37.4	37.5			-4 4.4	2.3		
		-3 38.4	39.5			-5 40.3	39.0			0 11.6	11.1			3 62.4	61.8			-5 14.1	14.6			-3 28.9	28.7		
		-2 20.0	19.1			-4 61.9	59.7			-1 9.5	9.2			4 13.3	13.0			-4 17.7	16.3			-2 19.4	18.8		
		-1 21.0	21.6			-3 16.0	14.7			2 25.2	25.0			5 14.8	15.2			-3 12.4	11.0			-1 59.1	60.0		
		0 37.7	36.6			-2 61.2	59.7			3 9.2	11.4	5 13	-7	42.9	44.6			-2 51.0	50.1			0 31.3	30.4		
		1 36.0	34.3			-1 41.1	39.7	4 24	-4	21.															

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

SiO ₄ 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 ₄ 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 ₆ 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 ₄ 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 ₄ 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		

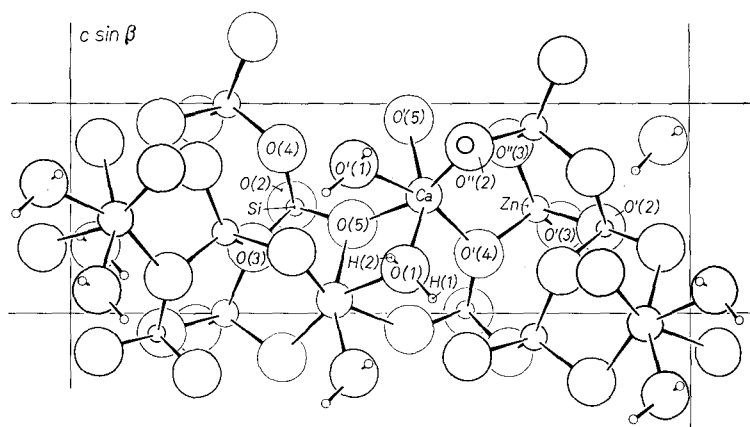


Fig. 1. Projection of the structure of clinohedrite along [100] on a perpendicular plane. The atoms of the asymmetric unit are labeled. The primed atoms are the symmetry-equivalent atoms shown in Fig. 3

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:

