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The crystal structure of laurionite, Pb(OH)Cl

By **C. Ch. Venetopoulos** and **P. J. Rentzeperis**

Applied Physics Laboratory, Aristotle University of Thessaloniki

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Auszug

Die Kristallstruktur des Laurionits, Pb(OH)Cl, wurde mit Hilfe dreidimensionaler Diffraktometer-Daten (Philips PW 1100) bestimmt. Sie ist von derjenigen von Goldsztaub (1939) und Brasseur (1940) wesentlich verschieden. Die Gitterkonstanten, ermittelt nach der Methode der kleinsten Quadrate mit direkt auf dem Diffraktometer gemessenen θ-Werten, sind: $a = 9{,}6987$, $b = 4{,}0203$, $c = 7{,}1110$ Å; $Z = 4$, Raumgruppe *Pcmn*. Atomparameter und anisotrope Temperaturfaktoren wurden nach der Methode der kleinsten Quadrate bis zu $R = 0{,}057$ verfeinert.

Jedes Pb-Atom wird von fünf Cl-Atomen im Abstand von 3,112—3,344 Å und drei OH-Gruppen im Abstand von 2,355—2,441 Å umgeben. Vier der Cl-Atome bilden ein Rechteck parallel zur b-Achse und die drei OH-Gruppen mit dem fünften Cl-Atom formen ein verzerrtes, nicht ganz planares Viereck, dessen eine Diagonale parallel zu b verläuft. Das von beiden Vierecken begrenzte Polyeder ist ein stark verzerrtes quadratisches Antiprisma. Die Cl-Atome werden von fünf Pb-Atomen umgeben, welche die Ecken einer Pyramide besetzen, deren Basis ein Rechteck parallel zu b ist. Schließlich, werden die O-Atome tetraedrisch von drei Pb- und einem H-Atom umgeben. Die drei Pb-Atome bilden ein gleichschenkliges Dreieck, dessen Basis auch parallel zu b verläuft.

Die Atome der asymmetrischen Einheit liegen auf Symmetrie-Ebenen in $b/4$; folglich kann man die Elementarzelle als aus zwei Atom-Schichten parallel (010), im Abstand $b/2$ voneinander, betrachten. Innerhalb der Schichten gibt es keine regelmäßige Kugelpackung. Die Koordinations-Polyeder um die Pb-Atome bilden Zickzack-Ketten parallel zur c-Achse. Es besteht keine Isotypie zwischen Laurionit und Cotunnit, $PbCl_2$, wie es bisher angenommen wurde.

Abstract

The crystal structure of laurionite, Pb(OH)Cl, has been determined using three-dimensional intensities, measured with an automated Philips PW 1100 single-crystal diffractometer. The structure differs substantially from that proposed by Goldsztaub (1939) and Brasseur (1940). The cell constants, obtained by least-squares from direct θ-value measurements on the diffractometer, are: $a = 9.6987$, $b = 4.0203$, $c = 7.1110$ Å, $Z = 4$. The space group is

Pcmn. Atomic parameters and anisotropic temperature factors were refined by least-squares to $R = 0.057$.

Each Pb atom is surrounded by five Cl atoms at distances 3.112—3.344 Å and three OH groups at distances 2.355—2.441 Å. The four Cl atoms form a rectangle, parallel to *b*, while the three OH groups form with the fifth Cl atom a distorted nonplanar quadrilateral, one diagonal of which is parallel to *b*. The polyhedron is a strongly distorted square antiprism. The Cl atoms are surrounded by five Pb atoms at the vertices of a pyramid, whose base is a rectangle parallel to *b*. Finally, the O atoms are tetrahedrally surrounded by three Pb atoms and one H. The three Pb atoms form an isosceles triangle with its base also parallel to *b*.

The atoms of the asymmetric unit lie on the symmetry plane at $b/4$, so consequently the unit cell may be considered as consisting of two layers of atoms, parallel to (010) at a separation of $b/2$. Within the layers there is no regular closest packing. The coordination polyhedra around Pb order themselves in zig-zag chains parallel to *c*. Laurionite is not isotypic with $PbCl_2$, as previously supposed.

Introduction

Laurionite, $Pb(OH)Cl$, is an orthorhombic secondary mineral, formed in cavities of ancient lead slags exposed to the action of sea water at Laurion, Greece. It is usually found in association with other lead oxychlorides, such as paralaurionite, $Pb(OH)Cl$, penfieldite, $Pb_2(OH)Cl_3$, and fiedlerite, $Pb_3(OH)_2Cl_4$. The mineral was first identified and described by Köchlin (1887) and later studied by various other investigators (see Dana, 1951).

Cell constants and space group were first determined by Goldsztaub (1937) and subsequently by Brasseur (1940) and Strunz and Tennyson (1956). An approximate crystal-structure model was proposed by Goldsztaub (1937, 1939) and a slightly improved one, at least as regards the position of the lead atoms, by Brasseur (1940). The positions of the Cl and O atoms were inferred from spatial considerations. In both structures, however, the unacceptably long Pb—O and O—O distances (see Table 6) indicated that the O atoms had been wrongly placed. Also, in view of the OH groups present, the 9 coordination around the Pb atom could not be considered very probable, as in the seemingly analogous case of $PbCl_2$ (Bräkken, 1932; Sahl and Zemann, 1961). A doubt as to the correctness of the structure was already expressed in the *Strukturbericht* (1939).

The determination of the correct structure of laurionite was undertaken as part of a larger program of systematic investigation of the partially known or unknown structures of the lead oxyhalides in the slags of Laurion.

Experimental

Well-developed needles of laurionite were singled out of the lead slags. As they highly absorb the x-rays, several attempts were made to shape them into small spheres, but, owing to cleavage, this proved impossible. Finally, a small prism, 1.1 mm in length and of trapezoidal cross-section (average dimensions 0.07 × 0.05 mm), was selected.

The crystal was centered on a computer-controlled Philips PW 1100 four-circle single-crystal diffractometer and the cell constants were determined first by using the peak-hunting routine and then the lattice-constants routine of the instrument. In view of the appreciable differences between the two sets of values, the θ angles of 36 strong reflections and their symmetry-equivalents (186 in all) were directly measured on the diffractometer and subsequently used in the least-squares program PARAM (STEWART *et al.*, 1972) for accurate cell-parameter determination. The final values obtained are given in Table 1, together with those of GOLDSZTAUB (1937) and STRUNZ and TENNYSON (1956) for comparison. The orientation of the unit cell corresponds to that adopted by STRUNZ and TENNYSON, which allows immediate comparison to the monoclinic paralaurionite.

Systematic absences indicated two possible space groups: *Pcmn* and $Pc2_1n$. Although intensity statistics favoured the noncentrosymmetric space group, yet, owing to the fact that all the atoms in the asymmetric unit happen to have $y = \frac{1}{4}$ (Table 2), the final structure could equally well be explained by both space groups. In the absence of any indication for pyroelectricity or piezoelectricity the holohedral

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

	VENETOPOULOS and RENTZEPERIS (this paper)	STRUNZ and TENNYSON (1956)	GOLDSZTAUB* (1937) (reoriented)
a	9.6987(15) Å	9.62 Å	9.7 Å
b	4.0203(8)	4.03	4.05
c	7.1110(9)	7.12	7.1
V	277.270 Å^3	276.03 Å^3	278.9 Å^3
Z	4	4	4

$\varrho_{\text{meas}} = 6.241\ \text{g} \cdot \text{cm}^{-3}$ (DE SCHULTEN, 1897).
$\varrho_{\text{calc}} = 6.212\ \text{g} \cdot \text{cm}^{-3}$.
Space group: *Pcmn*.

space group was finally adopted, in agreement with GOLDSZTAUB and BRASSEUR, whose orientation, however, was *Pnam*.

Three-dimensional intensity data were collected on the PW 1100 diffractometer in the ω-scan mode, using Mo$K\alpha$ radiation monochromated with a graphite monochromator. At first the intensities of 686 independent reflections in the asymmetric unit of the reciprocal lattice were measured, but it proved impossible to obtain an R value lower than 0.11. As it became obvious that the usual absorption correction in the case of a highly absorbing crystal ($\mu = 607.7\ \mathrm{cm}^{-1}$) with nonspherical or noncylindrical shape would not lead to further refinement, an attempt was made to overcome this obstacle by measuring all the symmetrical reflections as well. The 4646 measured reflections were averaged to a set of 686 nonequivalent ones; these readily yielded $R = 0.057$. Obviously, since the method gave very satisfactory results in a rather extreme case, it is very probable that it may be quite suitable for cases where accurate absorption correction is mandatory but not otherwise achievable.

Integrated intensities were converted to $|F_o|$ values in the usual way. For all subsequent computations the programs incorporated in the *X-ray System of crystallographic programs* (STEWART *et al.*, 1972) were used throughout.

Determination of the structure and refinement

The approximate structural model proposed by GOLDSZTAUB (1939), as modified by BRASSEUR (1940), was used as a starting point for the accurate structure determination. In these models all atoms occupy the special position $4c$: $x, \frac{1}{4}, z$; $\frac{1}{2} - x, \frac{1}{4}, \frac{1}{2} + z$ and their inversion set of space group *Pcmn*, with coordinates given in Table 3. Structure-factor calculations, using these parameters and an isotropic temperature factor $B = 1$ for each of the atoms, gave $R = 0.233$ for the Goldsztaub model and 0.185 for the Brasseur model.

Refinement of the structure was carried out by least squares, using the program CRYLSQ of the *X-ray System* (STEWART *et al.*, 1972). Fully ionized state for all atoms (except H), was assumed and probable isotropic temperature factors were assigned to them. Atomic-form factors, and also anomalous-dispersion corrections for the Pb and Mn atoms, were obtained from the *International tables* (1968). A single scale factor was used for the whole set of reflection data.

Refinement with isotropic temperature factors reduced R to 0.13. Then anisotropic temperature coefficients were introduced; in ten

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

Atom	x	y	z	B
Pb	0.08770(7)	$\frac{1}{4}$	0.79736(9)	1.32(2) Å^2
Cl	0.8202(4)	$\frac{1}{4}$	0.5564(6)	1.16(12)
O	0.0422(13)	$\frac{1}{4}$	0.122(2)	1.2(4)
H	0.110	$\frac{1}{4}$	0.223	3

Table 3

Comparison between atomic coordinates found for laurionite by various investigators

Atom	Coordinate	Venetopoulos and Rentzeperis* (this paper)	Goldsztaub (1939) (reoriented to *Pcmn*)	Brasseur (1940) (reoriented to *Pcmn*)
Pb	x	0.08770	0.088	0.088
	y	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
	z	-0.20264	-0.21	-0.204
Cl	x	-0.1798	-0.174	-0.185
	y	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
	z	-0.4436	-0.465	-0.469
O	x	0.0422	0.088	0.125
	y	$\frac{1}{4}$	$\frac{1}{4}$	$\frac{1}{4}$
	z	0.1223	0.16	0.169
H	x	0.110		
	y	$\frac{1}{4}$		
	z	0.223		

* To facilitate comparison, atomic coordinates corresponding to the atoms in the next two columns are given and not to those in Table 2.

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

Temperature factor $= \exp - (h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pb	48(1)	112(3)	69(1)	0	27(1)	0
Cl	37(3)	134(17)	60(6)	0	3(4)	0
O	25(10)	5(5)	121(26)	0	6(13)	0

Table 5. *Observed and calculated structure factors for laurionite*

h k l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h k l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h k l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h k l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h k l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h k l	$\lvert F_o \rvert$	$\lvert F_c \rvert$
0 0 2	200.2	198.9	2 0 4	27.4	30.0	3 3 6	22.5	22.1	5 1 7	53.1	50.1	7 0 6	51.5	50.5	9 0 6	96.0	97.4
4	80.5	76.8	5	13.0	9.9	7	23.7	22.4	8	18.5	19.3	7	78.4	73.9	7	20.3	14.1
6	26.4	21.2	6	19.8	14.3	8	63.6	66.0	9	75.1	71.3	8	34.8	30.4	8	52.8	52.0
8	96.4	99.8	7	53.5	56.0	9	19.0	10.1	10	21.7	17.0	9	45.6	40.5	9	23.6	23.9
10	63.9	67.3	8	18.1	17.3	3 4 1	22.1	18.2	5 2 1	81.1	75.1	10	8.7	4.6	9 1 0	117.0	110.5
0 1 2	103.8	98.0	9	74.9	78.6	2	76.4	73.2	2	12.9	10.1	7 1 0	141.1	133.4	1	28.4	27.6
4	232.9	237.3	10	41.0	41.4	3	23.0	19.8	3	116.8	116.8	1	129.0	125.3	2	113.9	116.2
6	148.9	144.2	11	56.7	60.6	4	118.8	123.5	4	66.2	64.2	2	66.8	66.0	3	16.4	14.6
8	85.5	84.6	2 1 1	127.5	119.5	5	19.9	16.3	5	133.7	129.0	3	82.2	83.5	4	45.9	47.9
10	14.0	15.9	2	61.9	62.6	6	99.1	101.0	6	48.2	44.7	4	31.9	30.3	5	33.3	36.3
0 2 0	313.6	315.0	3	152.3	158.2	7	9.8	7.5	7	100.5	95.0	5	27.4	26.1	6	20.6	19.0
2	158.2	167.3	4	63.9	65.2	8	53.1	54.9	8	42.9	39.7	6	28.4	25.7	7	25.3	24.6
4	70.0	66.9	5	148.7	156.0	3 5 0	119.7	131.9	9	21.5	15.6	7	27.3	23.0	8	42.7	39.9
6	22.5	19.0	6	90.9	90.2	1	19.4	17.9	10	21.5	20.2	8	75.2	69.7	9	23.0	23.5
8	85.4	90.3	7	108.8	113.7	2	96.4	94.7	5 3 0	93.3	86.5	9	45.0	43.2	9 2 1	27.7	24.6
10	58.4	62.0	8	37.2	37.6	3	19.9	15.0	1	146.0	139.5	10	38.4	33.2	2	75.5	75.3
0 3 2	78.3	79.5	9	23.7	23.1	4	34.1	36.2	2	44.7	42.8	7 2 1	34.5	31.7	3	19.5	21.8
4	172.1	178.5	10	11.8	8.2	5	12.6	4.2	3	100.3	97.5	2	56.5	55.5	4	76.1	80.9
6	115.8	115.1	11	12.0	4.4	6	23.3	15.6	4	28.0	27.8	3	77.7	79.2	5	26.1	25.6
8	70.0	70.0	2 2 0	108.4	100.2	3 6 1	14.0	10.8	5	16.3	12.5	4	103.7	105.8	6	87.4	88.7
10	10.0	13.7	1	181.5	186.0	2	47.4	46.4	6	19.2	12.7	5	89.4	88.1	7	19.8	12.8
0 4 0	214.1	198.1	2	108.2	103.8	3	16.8	12.0	7	42.2	41.6	6	47.9	45.9	8	48.5	47.8
2	107.7	113.0	3	142.5	140.1	4 0 0	152.8	152.2	8	19.4	15.9	7	71.5	67.3	9 3 0	95.4	89.8
4	46.2	47.9	4	26.7	27.2	1	188.4	197.6	9	61.4	60.2	8	31.8	27.8	1	24.4	22.4
6	19.1	14.3	5	11.1	8.5	2	110.4	107.8	5 4 1	54.0	52.2	9	39.6	37.3	2	93.3	94.4
8	61.7	68.6	6	14.9	12.7	3	95.2	95.7	2	14.1	8.4	7 3 0	112.8	104.8	3	18.1	11.9
0 5 2	55.3	52.7	7	48.9	50.3	4	42.0	37.2	3	86.3	83.9	1	101.9	98.5	4	36.8	39.6
4	110.4	118.9	8	16.9	15.8	5	59.5	52.6	4	45.3	46.5	2	53.6	52.3	5	29.6	30.0
6	75.7	80.8	9	70.1	71.9	6	33.6	32.0	5	94.4	95.7	3	64.8	66.5	6	21.7	15.8
0 6 0	122.1	122.5	10	36.7	38.0	7	59.5	55.4	6	35.1	34.0	4	26.1	24.1	7	22.9	20.9
2	72.7	71.5	2 3 1	87.0	77.4	8	64.1	60.7	7	73.3	72.3	5	22.6	21.3	9 4 1	25.0	18.1
4	31.9	30.2	2	50.8	47.3	9	64.1	62.0	8	34.0	30.7	6	21.8	21.4	2	53.8	56.5
1 0 1	70.1	72.6	3	119.0	117.1	10	41.8	42.7	5 5 0	57.2	56.9	7	22.0	19.2	3	19.7	16.6
2	108.9	110.9	4	52.5	50.5	11	41.8	41.6	1	91.1	93.2	8	60.5	58.5	4	57.7	62.1
3	188.2	191.7	5	123.7	122.6	4 1 1	32.2	28.4	2	27.8	29.0	7 4 1	23.0	22.9	5	19.7	19.9
4	80.9	78.7	6	72.4	71.9	2	89.4	85.2	3	63.9	65.8	2	41.4	40.5	6	64.9	68.4
5	158.7	160.8	7	89.2	92.3	3	146.6	150.1	4	18.0	19.0	3	56.8	58.4	9 5 0	66.1	63.3
6	107.8	105.7	8	32.4	31.2	4	117.5	113.1	5	12.6	8.2	4	75.5	78.6	1	24.3	16.1
7	92.0	95.5	9	27.0	19.7	5	135.2	132.5	6	12.4	8.8	5	64.9	66.6	2	62.4	66.3
8	32.8	34.1	10	8.1	6.9	6	76.9	73.4	5 6 1	29.7	32.7	6	36.8	35.4	3	21.5	7.8
9	47.1	48.2	2 4 0	69.3	64.9	7	76.9	74.6	2	14.2	5.4	7	52.8	52.1	10 0 0	87.9	85.6
10	2.7	1.9	1	132.7	125.9	8	34.4	33.8	6 0 0	176.4	175.5	7 5 0	73.3	70.9	1	81.4	76.1
1 1 0	123.4	111.7	2	72.8	69.4	9	58.1	55.9	1	48.4	44.6	1	67.1	67.4	2	59.1	59.2
1	210.8	223.3	3	94.9	95.8	10	13.5	3.6	2	176.7	181.3	2	36.0	36.4	3	65.0	70.6
2	147.6	149.4	4	23.6	20.1	4 2 0	135.1	127.0	3	17.8	14.9	3	44.5	46.2	4	19.5	17.9
3	131.1	128.9	5	10.3	5.9	1	173.7	166.1	4	61.0	59.7	4	23.1	17.1	5	8.1	7.3
4	32.1	30.7	6	13.4	9.3	2	95.4	91.0	5	17.2	14.9	5	22.3	15.1	6	28.8	28.4
5	38.8	33.7	7	38.4	38.2	3	84.8	82.4	6	35.0	32.4	8 0 0	82.8	76.7	7	8.5	0.3
6	33.9	34.0	8	16.8	12.3	4	34.7	31.8	7	34.0	32.0	1	151.7	152.1	8	50.9	52.1
7	63.9	64.2	2 5 1	50.6	49.0	5	50.8	45.9	8	58.4	52.2	2	25.7	27.4	10 1 1	37.9	34.4
8	29.2	29.7	2	32.2	31.1	6	28.1	28.7	9	26.1	21.0	3	67.0	68.8	2	54.7	53.5
9	70.0	73.2	3	73.7	77.4	7	53.0	49.9	10	75.3	72.9	4	31.0	34.0	3	37.7	40.1
10	47.6	51.5	4	30.4	34.3	8	57.9	55.3	6 1 1	11.6	7.5	5	8.8	6.2	4	66.8	76.1
11	44.3	49.5	5	80.7	84.0	9	58.2	56.7	2	121.1	118.5	6	25.3	26.8	5	58.9	60.8
1 2 1	66.8	57.5	6	48.3	49.9	10	42.0	39.3	3	33.1	32.4	7	54.6	52.1	6	45.5	47.4
2	93.1	87.6	7	59.6	64.8	4 3 1	23.4	21.5	4	120.9	122.5	8	16.1	9.9	7	64.7	63.4
3	158.9	156.8	2 6 0	44.3	41.2	2	66.4	62.7	5	35.4	32.5	9	62.6	60.9	8	22.3	19.2
4	71.0	69.0	1	79.8	79.1	3	114.9	112.6	6	142.2	136.3	8 1 1	32.4	30.5	10 2 0	79.3	77.2
5	138.6	140.8	2	42.3	43.3	4	88.4	88.2	7	6.4	0.4	2	11.4	3.9	1	72.8	68.6
6	93.5	93.5	3	52.5	60.6	5	105.0	105.6	8	66.7	61.9	3	101.5	106.8	2	53.0	53.5
7	81.4	85.8	4	26.6	12.7	6	61.3	59.6	9	15.2	9.8	4	46.4	46.8	3	60.3	63.8
8	29.8	31.0	3 0 1	57.0	47.9	7	61.9	61.6	10	16.2	10.5	5	114.1	115.5	4	17.3	16.3
9	40.6	43.9	2	116.3	121.2	8	30.6	28.2	6 2 0	160.5	152.0	6	27.5	24.8	5	13.0	6.8
10	3.8	1.6	3	34.9	33.2	9	47.5	46.8	1	40.7	37.5	7	74.4	69.4	6	26.2	26.1
1 3 0	97.8	83.2	4	193.4	200.7	4 4 0	91.3	87.3	2	158.6	156.8	8	40.5	37.7	7	9.6	0.3
1	159.6	160.6	5	29.5	26.5	1	115.8	114.9	3	13.8	12.1	9	28.3	24.7	8	47.4	48.0
2	104.9	102.4	6	151.1	152.2	2	66.7	63.1	4	54.4	52.8	8 2 0	73.1	67.3	10 3 1	28.1	28.0
3	95.8	94.1	7	13.2	11.6	3	57.9	58.1	5	17.0	13.2	1	140.9	134.3	2	42.6	44.1
4	27.1	23.8	8	79.0	78.5	4	23.3	22.5	6	32.2	29.2	2	25.8	24.5	3	32.9	33.3
5	26.5	25.6	9	13.2	4.5	5	32.0	33.3	7	30.5	29.0	3	59.4	61.7	4	55.6	63.3
6	25.3	27.1	10	17.5	13.6	6	25.5	21.5	8	50.4	47.9	4	29.9	30.6	5	47.4	51.1
7	49.5	52.2	11	19.3	19.2	7	37.8	37.8	9	21.1	19.2	5	9.8	5.6	6	37.4	39.9
8	32.0	24.9	3 1 0	273.2	294.1	8	41.9	42.7	10	68.1	67.0	6	25.2	24.3	7	52.2	53.5
9	57.5	61.4	1	54.3	44.1	4 5 1	18.6	14.4	6 3 1	10.6	4.2	7	49.5	47.5	10 4 0	60.2	58.2
10	37.8	43.3	2	189.8	196.3	2	43.9	41.5	2	93.1	91.7	8	16.5	8.9	1	53.7	52.3
1 4 1	39.8	36.5	3	39.1	35.4	3	72.1	75.3	3	26.3	25.9	9	55.7	56.0	2	40.3	40.8
2	58.2	58.4	4	69.9	68.5	4	57.9	60.0	4	98.5	98.1	8 3 1	25.2	24.7	3	43.6	48.3
3	102.2	106.1	5	14.8	9.0	5	67.4	72.9	5	27.9	26.1	2	8.9	2.8	4	16.0	12.8
4	49.8	49.2	6	29.7	27.3	6	41.5	42.0	6	114.9	111.7	3	80.7	86.5	5	11.4	5.7
5	97.6	101.9	7	27.3	27.5	4 6 0	49.5	55.0	7	8.1	0.2	4	37.6	37.9	11 0 1	13.5	10.0
6	65.1	68.8	8	77.6	79.6	1	68.2	72.5	8	54.5	52.1	5	93.7	95.3	2	9.3	5.4
7	59.3	64.8	9	12.1	12.1	2	42.7	40.4	9	13.6	8.5	6	23.4	21.0	3	73.2	78.1
8	26.8	23.9	10	69.8	70.9	3	34.3	38.4	6 4 0	113.9	108.3	7	61.5	58.4	4	12.0	8.3
9	31.6	34.0	11	8.7	2.1	5 0 1	93.5	90.0	1	27.3	26.1	8	32.8	31.8	5	77.7	85.1
1 5 0	59.6	53.3	3 2 1	37.3	31.0	2	10.2	9.0	2	108.9	112.3	8 4 0	49.6	49.2	6	18.8	22.1
1	110.1	103.6	2	109.6	104.6	3	125.9	134.2	3	16.1	8.3	1	100.6	99.0	7	48.6	46.7
2	64.0	65.8	3	29.3	28.0	4	75.9	73.5	4	39.7	39.0	2	19.2	18.5	8	28.9	26.6
3	57.3	61.8	4	166.7	173.3	5	151.7	145.3	5	17.0	10.1	3	43.6	46.3	11 1 0	21.4	18.2
4	17.9	16.1	5	25.5	22.8	6	55.5	49.9	6	25.2	21.9	4	25.4	23.0	1	103.8	101.7
5	23.7	17.3	6	134.9	135.4	7	112.9	105.0	7	25.7	22.0	5	9.8	4.0	2	24.6	25.7
6	19.2	18.5	7	12.8	10.4	8	46.7	43.6	6 5 1	9.3	2.6	6	24.7	18.5	3	35.5	36.3
7	35.2	36.9	8	72.3	71.3	9	20.0	16.9	2	59.7	62.0	8 5 1	20.1	17.3	4	21.3	25.5
1 6 1	29.3	23.2	9	12.3	3.9	10	21.2	22.0	3	22.4	17.6	2	7.6	1.7	5	11.9	11.9
2	37.2	36.2	10	15.5	12.4	5 1 0	128.6	120.3	4	67.7	68.7	3	56.2	60.4	6	20.1	19.4
3	59.1	67.3	3 3 0	210.7	205.0	1	185.6	184.6	5	20.4	18.5	4	27.9	26.2	7	40.3	40.2
4	31.5	32.4	1	32.5	28.3	2	58.2	55.1	7 0 1	38.5	36.4	9 0 1	29.2	27.5	11 2 1	17.7	9.2
2 0 0	121.6	124.0	2	144.9	144.2	3	124.2	126.0	2	65.7	63.7	2	83.5	84.3	2	9.7	4.9
1	212.6	222.1	3	24.1	23.5	4	35.4	34.3	3	87.6	89.7	3	23.0	24.1	3	66.9	71.0
2	125.7	129.8	4	54.5	53.7	5	20.6	15.9	4	114.0	118.7	4	82.1	89.5	4	13.0	7.6
3	160.5	170.2	5	13.2	7.1	6	17.2	15.6	5	99.3	98.0	5	27.6	28.2	5	70.4	77.9

Table 5. *(Continued)*

h k l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h k l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h k l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h k l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h k l	$\lvert F_o \rvert$	$\lvert F_c \rvert$	h k l	$\lvert F_o \rvert$	$\lvert F_c \rvert$
11 2 6	24.4	20.3	12 0 2	61.7	61.7	12 2 2	56.9	56.4	13 0 3	23.6	21.5	13 2 5	32.3	35.0	14 2 0	9.0	5.7
7	44.3	43.2	3	14.8	15.3	3	16.5	13.8	4	38.4	41.0	13 3 0	38.8	36.4	1	52.8	54.7
11 3 0	18.2	15.2	4	34.5	37.8	4	30.6	34.7	5	34.4	37.8	1	37.6	38.1	2	23.9	18.5
1	85.2	84.3	5	24.8	28.9	5	21.3	26.4	6	39.5	44.8	2	36.6	41.1	3	29.4	29.3
2	24.4	21.4	6	6.2	3.0	6	7.3	2.8	13 1 0	43.5	42.8	3	31.8	31.6	15 0 1	12.6	8.3
3	28.5	30.5	7	22.8	24.9	12 3 1	21.9	20.2	1	45.0	45.0	14 0 0	3.9	6.3	2	16.7	19.6
4	22.2	21.4	12 1 1	24.1	24.4	2	33.4	34.3	2	48.3	48.9	1	58.5	59.4	3	22.3	24.4
5	12.8	9.6	2	39.7	40.5	3	20.8	19.5	3	36.5	37.7	2	23.6	20.2	15 1 0	49.5	51.7
6	18.9	16.4	3	23.0	23.1	4	52.5	58.4	4	12.6	7.3	3	30.3	31.8	1	14.6	17.2
11 4 1	14.7	7.3	4	62.5	69.5	5	17.9	18.4	5	14.2	11.4	4	22.1	18.7	2	32.1	32.0
2	9.5	3.8	5	22.7	21.7	12 4 0	59.6	59.7	6	26.4	26.1	5	6.7	1.4			
3	48.9	54.5	6	46.6	51.8	1	17.3	15.0	13 2 1	16.9	11.9	14 1 1	21.3	15.3			
4	13.4	6.0	7	13.4	11.3	2	42.9	44.1	2	37.1	40.5	2	12.8	7.5			
12 0 0	87.2	85.5	12 2 0	79.0	77.8	13 0 1	15.7	13.1	3	19.5	19.8	3	40.2	43.3			
1	23.9	20.8	1	21.3	19.0	2	42.7	44.2	4	34.5	37.8	4	9.1	8.5			

further cycles the refinement of the atomic parameters practically converged to $R = 0.058$.

At this stage an attempt was made to locate the H atom in the asymmetric unit. However, in the presence of the heavy Pb atoms no

Table 6. *Interatomic distances in laurionite with their standard deviations*
The indices in parentheses refer to the atoms in Figs. 2, 3 and 6

Central atom Pb(2)			
Pb(2)—Cl(2)	3.112(4) Å	Cl(4)—Cl(6)	3.812(6) Å
Cl(4)	3.197(3)	Cl(7)	4.020(3)
Cl(7)	3.197(3)	O(2)	3.598(11)
Cl(5)	3.344(3)	O(3)	3.549(13)
Cl(6)	3.344(3)		
O(2)	2.355(1)	Cl(5)—Cl(6)	4.020(3)
O(3)	2.441(7)	Cl(7)	3.812(6)
O(5)	2.441(7)	O(5)	3.767(12)
Cl(2)—Cl(5)	4.108(5)	Cl(6)—O(3)	3.767(15)
Cl(6)	4.108(5)		
O(3)	3.325(12)	Cl(2)—O(2)	3.598(11)
O(5)	3.325(12)	O(5)	3.549(13)
		O(2)—O(3)	2.784(15)
		O(5)	2.784(15)
Central atom Cl(4)			
Cl(4)—Pb(8)	3.112(4) Å	Pb(2)—Pb(6)	4.020(1) Å
Pb(2)	3.197(3)	Pb(8)	5.297(1)
Pb(6)	3.197(3)		
Pb(1)	3.344(3)	Pb(5)—Pb(6)	4.754(1)
Pb(5)	3.344(3)	Pb(8)	4.987(1)
Pb(1)—Pb(2)	4.754(1)	Pb(6)—Pb(8)	5.297(1)
Pb(5)	4.020(1)		
Pb(8)	4.987(1)		

Table 6. *(Continued)*

Central atom O(2)			
O(2)—Pb(2)	2.355(15) Å	Pb(3)—Pb(7)	4.020(1) Å
Pb(3)	2.441(7)	H(2)	2.78
Pb(7)	2.441(7)		
H(2)	0.97	Pb(7)— H(2)	2.78
Pb(2)—Pb(3)	3.907(1)		
Pb(7)	3.907(1)		
H(2)	3.04		

Table 7. *Bond angles in laurionite with their standard deviations*
The indices in parentheses refer to the atoms in Figs. 2, 3 and 5

Central atom Pb(2)		Central atom Cl(4)	
Cl(2)—Pb(2)—Cl(5)	78.93(10)°	Pb(1)—Cl(4)—Pb(2)	93.21(5)°
Cl(6)	78.93(10)	Pb(5)	73.91(9)
O(3)	72.42(32)	Pb(8)	101.07(10)
O(5)	72.42(32)		
		Pb(2)—Cl(4)—Pb(6)	77.93(10)
Cl(4)—Pb(2)—Cl(6)	71.24(9)	Pb(8)	114.17(11)
Cl(7)	77.93(7)		
O(2)	79.2(3)	Pb(5)—Cl(4)—Pb(6)	93.21(5)
O(3)	76.7(3)	Pb(8)	101.07(10)
Cl(5)—Pb(2)—Cl(6)	73.91(6)	Pb(6)—Cl(4)—Pb(8)	114.17(11)
Cl(7)	71.24(9)		
O(5)	79.6(3)	Central atom O(2)	
Cl(6)—Pb(2)—O(3)	79.6(3)	Pb(2)—O(2)—Pb(3)	109.1(4)
		Pb(7)	109.1(4)
		H(2)	126.6
Cl(7)—Pb(2)—O(2)	79.2(3)		
O(5)	76.7(3)	Pb(3)—O(2)—Pb(7)	110.9(5)
		H(2)	100.2
O(2)—Pb(2)—O(3)	70.9(4)		
O(5)	70.9(4)	Pb(7)—O(2)— H(2)	100.2

unambiguous position could be found on the Fourier and difference Fourier maps. Consequently its position was inferred from the following considerations: (*a*) In the OH group the average O—H distance is 0.97 Å; (*b*) as there are four H atoms in the unit cell, they should also occupy the special position 4*c* with $y = \frac{1}{4}$ or $\frac{3}{4}$ and; (*c*) as can be seen from Tables 6 and 7, each of the O atoms is bonded to three Pb atoms at almost equal distances while the angles Pb—O—Pb vary between 109.08° and 110.89°, *i. e.* they are almost equal to the central angles of a regular tetrahedron. Since in many structures O appears to be in the center of tetrahedron of cations, it was assumed that the H atom lay along the fourth bond direction of a regular tetrahedron around the O atom (at a distance of 0.97 Å), whose three vertices were occupied by the Pb atoms. The coordinates determined in this way, together with an isotropic temperature factor $B = 3$, were introduced in the CRYLSQ program. Further least-squares cycles were calculated with the H atom fixed at several positions near the one defined above. The coordinates in Table 2 gave a final $R = 0.057$.

The final atomic parameters are given in Table 2 and the anisotropic temperature coefficients β_{ij} in Table 4. In Table 3 the atomic coordinates are compared with those of previous investigators. Comparison between $|F_o|$ and $|F_c|$ values obtained with the parameters in Tables 2 and 4 is made in Table 5. Interatomic distances and angles are given in Tables 6 and 7, in which the indices in parentheses refer to the atoms in Figs. 2, 3 and 5.

Description of the structure and discussion

As all the atoms of the asymmetric unit lie on the symmetry plane at $\frac{1}{4}b$, repetition by the symmetry elements results in bringing half the unit-cell contents on the plane parallel to (010) at $\frac{1}{4}b$ and the other half on the parallel plane at $\frac{3}{4}b$. Consequently, the unit cell may be considered as made up of two layers, each with 2Pb(OH)Cl, parallel to (010) and separated by a distance $\frac{1}{2}b$, *i. e.* 2.01 Å. Owing to the symmetry center at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$, the atoms in the one layer are centrosymmetrical to corresponding atoms in the other. The atomic arrangement in the layers differs considerably from a hexagonal close-packed array, due to the difference in ionic radii between Cl and O. Figure 1 shows a projection of the structure parallel to *b* and Fig. 2 is a clinographic projection.

The structure may better be described in terms of the coordination polyhedra around the Pb atoms. As can be seen from Figs. 1 and 2, each Pb atom is surrounded by five Cl atoms and three OH groups. One of these polyhedra is shown in clinographic projection in Fig. 3. Four of the five Cl atoms of the polyhedron form a rectangle with sides 4.020 Å (= *b*) parallel to *b* and 3.812 Å at an angle of 20.95° to

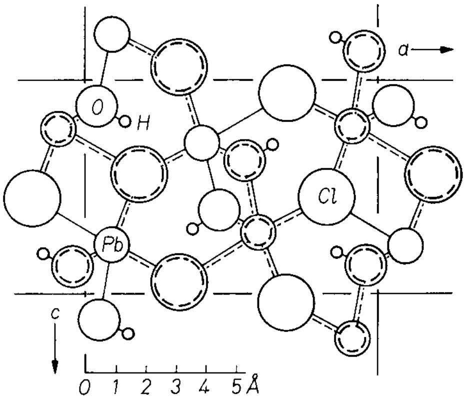

Fig. 1. Projection of the structure parallel to b. Single full circles represent atoms at $\frac{1}{4}\,b$, whereas the double circles represent two atoms, one at $-\frac{1}{4}\,b$ and one at $\frac{3}{4}\,b$. The atoms of the asymmetric unit are indicated with their symbols

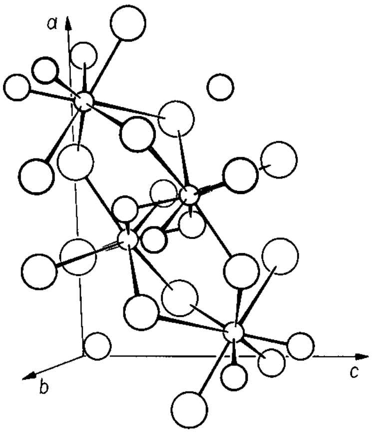

Fig. 2. Clinographic projection of laurionite

the c axis. The three O atoms with the fifth Cl atom form a nonplanar quadrilateral; one diagonal, namely O(3)—O(7) in Fig. 3, is parallel to b. The plane of the three O atoms is almost parallel to the rectangle of the four Cl atoms. The polyhedron is a strongly distorted square antiprism. The interatomic distances are indicated in Fig. 3.

The polyhedra around the Pb atoms share Cl—Cl edges parallel to b, and form zig-zag chains, whose mean directions are parallel to c.

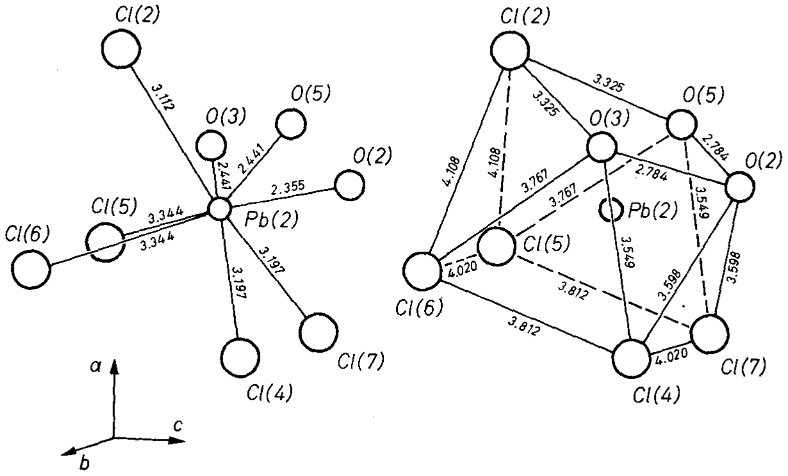

Fig. 3. Clinographic projection of the coordination polyhedron around the atom Pb(2) of Fig. 2

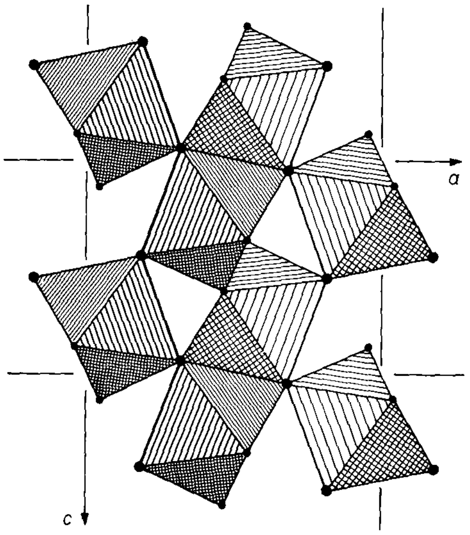

Fig. 4. Projection on (010) of the chains formed by edge-sharing $PbCl_5O_3$ polyhedra

As is shown in Fig. 4, two such chains, centrosymmetrical to each other, are formed in the unit cell at heights $\frac{1}{4}\,b$ and $\frac{3}{4}\,b$ respectively and they are linked together by common Cl and O atoms.

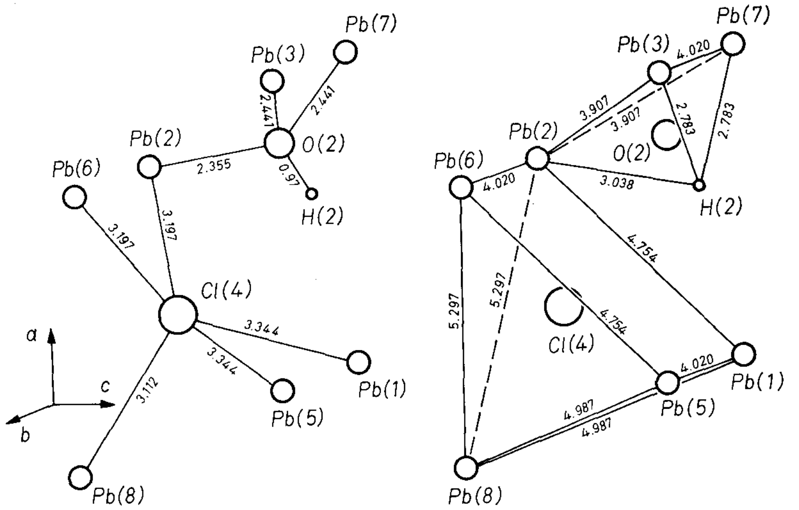

Fig. 5. Clinographic projection of the coordination polyhedra around the Cl(4) and O(2) atoms of Fig. 2

Each Cl atom is surrounded by five Pb atoms at the vertices of a pyramid, whose base is a rectangle parallel to *b*. As already explained, the O atoms are tetrahedrally surrounded by three Pb atoms and one H atom. Figure 5 shows the coordination polyhedra around the anions.

Table 8.

Comparison of interatomic distances in laurionite found by different investigators

Investigator	Pb—Cl	Pb—O	Cl—Cl	Cl—O	O—O
VENETOPOULOS and	3.112	2.355	3.812	3.325	2.784
RENTZEPERIS	3.197	2.441	4.020	3.549	
(this paper)	3.344		4.108	3.598	
				3.767	
GOLDSZTAUB (1939)	3.120	2.627	3.844	3.080	3.490
	3.313	2.672	4.050	4.113	
	3.181	3.276	3.968	3.369	
				3.681	
BRASSEUR (1940)	3.234	2.680	3.773	2.993	3.954
	3.217	2.885	4.030	4.345	
	3.217	2.905	4.114	3.071	
				3.942	

The final structure differs considerably from the models proposed by Goldsztaub (1939) and Brasseur (1940). From Table 4 it can be seen that the O position is quite different, while the Cl atoms are shifted to a lesser degree. As a result many interatomic distances show large differences in the two structures. Table 8 shows that the Pb—O and O—O distances in the models of Goldsztaub and Brasseur are unacceptably large, whereas some Cl—O distances are much smaller than the average values known from the literature. The nine-coordination polyhedron around the Pb atoms, formed by 5 Cl and 4 O atoms, so far accepted in the structure of laurionite, cannot be explained by the final structure. As mentioned above, an eight-coordination polyhedron, 5 Cl and 3 O atoms, is formed instead. The fourth O atom is at a distance 3.8 Å, too large to be accepted as a Pb—O bond distance, since the other three Pb—O distances are only 2.355 Å and 2.441 Å.

Based on the earlier structural model, Strunz and Tennyson (1956) were led to the conclusion that laurionite is isotypic with cotunnite, $PbCl_2$ (Bräkken, 1932; Sahl and Zemann, 1961). In view of the present results, however, this is not the case, although the two structures closely resemble each other. On the other hand, iodolaurionite, Pb(OH)I (Malčič and Zivadinovič, 1960) is isotypic with laurionite.

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