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The Crystal Structure of Lautite, CuAsS

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Lautite crystallizes in space group $Pna2_1$ of the orthorhombic system in a cell of dimensions $a=11.35$, $b=5.456$, $c=3.749$ Å. There are four formula units in the cell. The $hk0$ and $h0l$ data were collected with Mo $K\alpha$ radiation by film methods and were estimated photometrically. The structure was solved by Patterson methods and refined by both Fourier and least-squares techniques.

Lautite has a sphalerite derivative structure. The tetrahedral environment of each atom is as follows: Cu-3S, 1As: As-2As, 1Cu, 1S: S-3Cu, 1As. Bond distances and angles are normal and one interesting feature of the structure is the existence of infinite, planar, zigzag chains of arsenic atoms extending along a direction parallel to [001].

Introduction

Lautite (CuAsS) is a mineral found in very few occurrences, and derives its name from the type locality of Lautau, Saxony, where it occurs associated with native

arsenic, tennantite, proustite, chalcopyrite, galena and barite (Palache, Berman & Frondel, 1944). The same authors give the point group as $2/m 2/m 2/m$, which is not consistent with the space group $P2_12_12_1$ reported by Berry & Thompson (1962). No previous structure

determination is recorded, but Ross (1957) and Strunz (1957) classify lautite as having a sphalerite-type or related structure, which is unusual in sulphides having a metal to sulphur ratio of 2:1.

The present investigation was undertaken to resolve the point group – space group inconsistency, and to test the proposal of a sphalerite-type structure.

Experimental

A sample of lautite, from Lauta, Saxony, was kindly supplied by the Australian Museum. A small cleavage fragment of dimensions $0.15 \times 0.10 \times 0.07$ mm was examined by precession and equi-inclination Weissenberg photographs. The reciprocal lattice exhibits the Laue symmetry mmm and systematic absences occur for $0kl$ with $k+l \neq 2n$ and $h0l$ with $h \neq 2n$. The possible space groups are therefore $Pna2_1$, $Pnam$ and $P2_12_12_1$. The latter space group is not excluded by the systematic absences although it appears unlikely in view of the more general nature of the extinctions. However, it is included here as it has been proposed on the basis of powder work (Berry & Thompson, 1962). The single-crystal X-ray photographs gave no evidence of twinning. The cell dimensions, listed in Table 1, were obtained from zero level precession photographs using Mo $K\alpha$ radiation.

The crystal had been mounted about [100] and in view of the short lengths of the b and c axes it was decided to determine details of the structure from the $hk0$ and $h0l$ data. This data was conveniently recorded with the Buerger precession camera ($\mu = 30^\circ$, Mo $K\alpha$) utilizing a series of timed exposures which gave an interfilm density ratio of 10:1. The intensities were

measured photometrically and corrected for the polarization and asymmetric Lorentz factors using a transparent overlay based upon a chart prepared by Waser (1957). No corrections were made for absorption.

Determination of structure

A projection of the structure on to (001) will have a symmetry consistent with any of the three space groups listed above. The space groups in effect differ only in the distribution of the z coordinates of the symmetry related atoms. The c -axis Patterson projection could thus be unequivocally interpreted and use was made of the minimum function as described by Buerger (1950). Various choices of vectors for Patterson superposition invariably gave the same minimum function, but with respect to different origins. This trial structure, in which no distinction was initially made between Cu, As or S atoms, gave an initial R index of 0.64, but because of its recurrence an attempt was made to refine the associated atomic parameters. The refinement was carried out by a least-squares procedure in which $\sum w(|F_o| - |F_c|)^2$ was minimized. Each reflexion was weighted as follows: $|F_o| \leq 6 F_{\min}$, $w = (|F_o|/6 F_{\min})^2$; $|F_o| > 6 F_{\min}$, $w = (6 F_{\min}/|F_o|)^2$. A series of refinement cycles, in which an isotropic thermal parameter ($B = 2.0 \text{ \AA}^2$) was nominally applied to each atom, converged to an R value of 0.18. At an early stage during this refinement a distinction was made between copper, arsenic and sulphur atoms in the following manner: an average scattering curve $(f_{\text{As}} + f_{\text{Cu}} + f_{\text{S}})/3$ was used for each atom to calculate values of F_c . Phases were then assigned to the observed data and a (001) Fourier synthesis computed. The peak heights in this electron density map were found to be proportional to the atomic numbers of the three components As, Cu and S. Confirmation of the choice of atomic sites was later obtained in plausible values for the thermal parameters and a stereochemistry involving zigzag \ As / As \ chains rather than \ Cu / Cu \ chains. The reliability index was reduced to $R = 0.10$ when anisotropic thermal parameters of the form

Table 1. *Crystal data*

CuAsS, M.W. 170.5	
Orthorhombic	
$a = 11.35$, $b = 5.456$, $c = 3.749 \text{ \AA}$	
(accurate to 0.5%)	
$U = 232.16 \text{ \AA}^3$, $D_m = 4.91$, $D_x = 4.88 \text{ g.cm}^{-3}$	
$\mu = 251 \text{ cm}^{-1}$	
$Z = 4$, space group $Pna2_1$	

Table 2. *Atomic parameters*

Atom	Position	x/a	$\sigma(x/a)$	y/b	$\sigma(y/b)$	z/c	$\sigma(z/c)$
Cu(0)	4(a)	0.32617*	0.0003	0.43823*	0.0009	0.22992*	0.0008
		0.32410†		0.43737†		0.23130‡	
		0.32509‡					
As(0)	4(a)	0.48668*	0.0003	0.14766*	0.0006	0.21867*	0.0006
		0.48569†		0.15048†		0.22000‡	
		0.48587‡					
S(0)	4(a)	0.16668*	0.0006	0.17903*	0.0019	0.21283*	0.0020
		0.16768†		0.18070†		0.22000‡	
		0.16344‡					
Atom		$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Cu		30	359	535	zero	183	-17
As		44	307	452	zero	40	12
S		35	433	219	zero	150	-12

* Values obtained from least-squares treatment of all data.

† Values obtained from $hk0$ data.

‡ Values obtained from $h0l$ data.

Table 3. *Observed reflexion amplitudes and calculated structure factors*

Within each group of constant k or l the columns contain, from left to right: h , l (or k), $10 F_o$ etc. Reflexions too weak to be observed (< 90 on this scale), or those cut off by the beam stop, are not entered under F_o .

$l = 0$				$k = 0$													
h	K	F_o	F_c	h	K	F_o	F_c	h	l	F_o	$ F_c $	A_o	β_o				
0	2		49	4	6	221	-189	9	2	398	-439	0	2	1574	1815	-1475	550
0	4	416	-504	4	7		12	9	3	350	351	0	4	799	808	589	-526
0	6	199	173	5	1	173	75	9	4		25	2	1	456	493	456	-19
1	2	141	151	5	2	371	-420	9	5		-7	2	2	203	234	-179	97
1	3	547	662	5	3	489	543	10	0	191	198	2	3	233	211	-233	8
1	4	513	558	5	4	317	-307	10	1	298	316	2	4	167	125	100	-133
1	5		37	5	5		14	10	2		-39	4	1	122	104	-116	-39
1	6	87	93	5	6		25	10	3	192	-189	4	2	357	331	-310	178
1	7	353	-227	5	7	342	-212	10	4	157	-150	4	3		89		
2	0	192	354	6	0	1186	1754	10	5	516	-362	4	4	167	175	107	-128
2	1		53	6	1	308	366	11	1	120	170	6	1	429	544	407	-135
2	2	421	-456	6	2	48	40	11	2	320	-308	6	2	1136	1282	-1073	374
2	3	498	537	6	3	203	205	11	3	222	216	6	3	377	333	-223	304
2	4	384	-434	6	4	369	-354	11	4	70	-81	6	4	645	634	493	-417
2	5	207	208	6	5	99	-98	11	5		-8	8	1	456	470	456	-20
2	6	275	232	6	6	168	129	12	0	669	678	8	2		43		
2	7		68	7	1	146	-175	12	1	342	318	8	3	319	261	-317	29
3	1	1078	-1597	7	2	124	-162	12	2		6	8	4		28		
3	2	255	-274	7	3	311	329	12	3	266	193	10	1	184	163	171	-67
3	3	599	671	7	4	515	533	12	4	193	-129	10	2	179	166	-155	91
3	4		14	7	5		35	13	1	71	-76	10	3	168	165	-103	133
3	5		15	7	6	178	152	13	2	249	-194	10	4	92	103	65	-66
3	6		28	8	0		58	13	3		49	12	1	538	482	511	-168
3	7		-81	8	1	192	228	13	4	494	343	12	2	553	556	-534	141
4	0	300	453	8	2	284	-312	14	0	187	-175	12	3	402	349	-240	322
4	1	225	275	8	3	338	366	14	1	208	145	14	1	293	239	293	9
4	2	229	-274	8	4	225	-235	14	2	174	-136	14	2	131	165	123	-44
4	3	416	-417	8	5		-15	14	3	223	175						
4	4	377	-374	8	6	229	155	15	1	316	-251						
4	5	368	-403	9	1	598	-747	15	2	331	-303						

$\exp \{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)\}$ were introduced for each atom and further least-squares cycles were run. The final coordinate shifts were much smaller than the corresponding standard deviations and final atomic parameters for the (001) projection are listed in Table 2.

The b -axis Patterson projection consisted essentially of strong positive regions parallel to the x direction and centred in the sections $z/c=0$ and $\frac{1}{2}$. All atoms comprising the structure are therefore situated in, or very close to, two planes normal to the z axis, and $c/2$ Å apart. Substitution of the relevant x coordinate values obtained from the $hk0$ data together with combinations of $\pm\frac{1}{4}$ for z required by the space group $Pnam$ gave R values in excess of 0.50, an indication that the correct space group was one of the non-centric members $Pna2_1$ or $P2_12_12_1$. Trial and error methods, in which the z parameter for arsenic was slightly off-shifted from $\frac{1}{4}$ and the z parameters for the other atoms were chosen at $\pm\frac{1}{4}$, finally yielded a trial model with an associated R value of 0.28.

The number of $h0l$ data is restricted by systematic absences and attempts to refine the atomic parameters of the trial model with diagonalized least-squares

Table 4. *Selected interatomic distances (Å) and angles (°) in 4 CuAsS*

Numbers in parenthesis following the atomic symbols denote the following symmetry transformation of the parameters in Table 1:

0: x, y, z	5: $1-x, \bar{y}, \frac{1}{2}+z$
1: $\bar{x}, \bar{y}, \frac{1}{2}+z$	6: $1-x, \bar{y}, z-\frac{1}{2}$
2: $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$	7: $x-\frac{1}{2}, \frac{1}{2}-y, z$
3: $\frac{1}{2}+x, \frac{1}{2}-y, z$	8: $\frac{1}{2}-x, y-\frac{1}{2}, \frac{1}{2}+z$
4: $\frac{1}{2}-x, \frac{1}{2}+y, z-\frac{1}{2}$	9: $\frac{1}{2}-x, y-\frac{1}{2}, z-\frac{1}{2}$

Following the distance or angle the number in parenthesis is the estimated standard deviation.

Cu(0) tetrahedron

Cu(0)-S(0)	2.300(11)	S(0)-Cu(0)-S(2)	114.4(4)
-S(2)	2.238(11)	S(0)-Cu(0)-As(0)	101.0(3)
-As(0)	2.416(6)	S(0)-Cu(0)-S(4)	110.5(3)
-S(4)	2.343(11)	As(0)-Cu(0)-S(2)	111.9(3)
		As(0)-Cu(0)-S(4)	109.1(3)
		S(2)-Cu(0)-S(4)	109.8(4)

As(0) tetrahedron

As(0)-Cu(0)	2.416(6)	Cu(0)-As(0)-S(3)	114.2(3)
-S(3)	2.252(10)	Cu(0)-As(0)-As(5)	120.2(2)
-As(5)	2.490(4)	Cu(0)-As(0)-As(6)	122.0(2)
-As(6)	2.490(4)	S(3)-As(0)-As(5)	99.7(3)
		S(3)-As(0)-As(6)	98.9(3)
		As(5)-As(0)-As(6)	97.7(1)

Table 4 (cont.)

S(0) tetrahedra			
S(0)-Cu(0)	2.300(11)	Cu(0)-S(0)-As(7)	117.2(5)
-As(7)	2.252(10)	Cu(0)-S(0)-Cu(8)	107.2(4)
-Cu(8)	2.343(11)	Cu(0)-S(0)-Cu(9)	110.8(5)
-Cu(9)	2.238(11)	As(7)-S(0)-Cu(8)	105.0(4)
		As(7)-S(0)-Cu(9)	106.7(4)
		Cu(8)-S(0)-Cu(9)	109.8(5)
Some short non-bonded approach distances (tetrahedral edges)			
S(0)-As(0)	3.637(10)	Cu(0)-S(3)	3.919(11)
-S(2)	3.813(14)	-As(5)	4.253(6)
-S(4)	3.814(14)	-As(6)	4.290(6)
As(0)-S(2)	3.856(10)	-As(7)	3.883(6)
-S(4)	3.877(10)	-Cu(8)	3.735(7)
S(2)-S(4)	3.814(14)	-Cu(9)	3.735(7)
As(7)-Cu(8)	3.646(6)	As(5)-S(3)	3.630(10)
-Cu(9)	3.602(6)	-As(6)	3.749(4)
Cu(8)-Cu(9)	3.749(7)	As(6)-S(3)	3.606(10)

methods were unsuccessful. The model was refined by electron-density projections on (010) and, finally, difference Fourier syntheses until there was no detectable improvement. The R value for the $h0l$ data reduced to 0.17.

In a final series of least-squares calculations, anisotropic vibration of the atoms was assumed (27 parameters) and all the scaled observed structure amplitudes were used. The final coordinates are listed in Table 2 and the resulting F_c values are listed for comparison with the scaled F_o values in Table 3. The overall R index, for observed reflexions only, is 0.137.*

Standard deviations of the coordinates have been calculated by Cruickshank's method (1949). The curvatures of the atoms were calculated by differentiating the expression for the Fourier function and then computing the double summations with the suitably modified Fourier coefficients. Computations were performed on UTECOM (a DEUCE machine) with programs written by Rollett (1961). The scattering factors used were those for As, Cu and S tabulated by Freeman & Watson (*International Tables for X-ray Crystallography*, 1962a). No dispersion corrections were applied to these scattering curves (maximum $\Delta f^1 = -0.4e$).

Description of the structure

Lautite has a sphalerite derivative structure. Each atom is tetrahedrally coordinated and the tetrahedra share corners to form an infinite three-dimensional network. The structure, seen in clinographic projection, is depicted in Fig. 1.

The copper atom is surrounded by one arsenic and three sulphur atoms. The tetrahedron is only slightly distorted, three of the angles showing no significant departure from the theoretical 109.5° . Copper may therefore be considered to be in the +1 oxidation state and to exhibit the spherically symmetrical d^{10} arrangement. The bond lengths indicate normal covalence

with the Cu(O)-S(2) and Cu(O)-As(O) distances agreeing well with the theoretical single covalent bond distances listed by Pauling (1947) (Cu-S, 2.213; Cu-As, 2.383 Å). The remaining two Cu-S bond distances are slightly longer than normal ($\Delta/\sigma = 8$ and 12).

Each sulphur atom is coordinated to one arsenic and three copper atoms and the distortion from tetrahedral symmetry is again real but only slight. The arsenic-sulphur bond length of 2.252(10) Å is in good agreement with similar distances of 2.23(5) Å observed in realgar, As_4S_4 and 2.25(5) Å in orpiment, As_4S_6 (*International Tables for X-ray Crystallography*, 1962b).

A feature of the structure is the existence of infinite zigzag chains of arsenic atoms extending along a direction parallel to (001). The As-As bonding distance in any chain is 2.490(4) Å. This is to be expected for normal covalent bonding and agrees well with similar distances reported for gaseous As_4S_4 (2.49(4) Å), solid

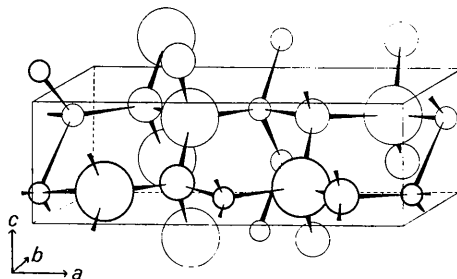


Fig. 1. The unit cell of lautite, CuAsS, seen in clinographic projection and showing the tetrahedral environment of each atom. The large open circles represent sulphur atoms, the medium open circles are copper atoms and the small circles represent arsenic atoms.

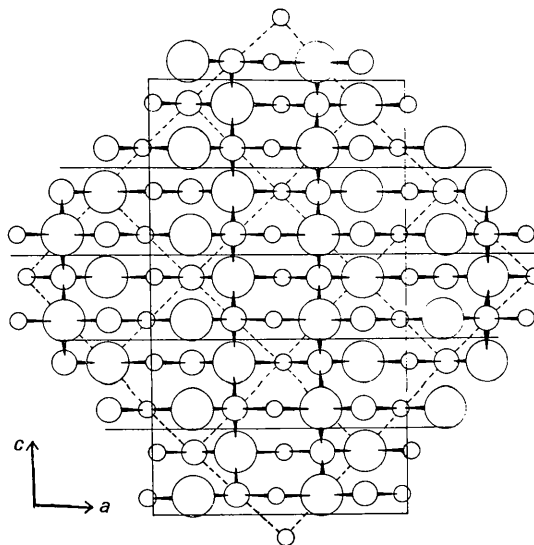


Fig. 2. Projection of the lautite structure on (010). The unit cells of lautite are outlined with unbroken lines whilst the related simple sphalerite cells are shown in dotted outline. The simplest repeating sphalerite macro-cell consists of a $3 \times 3 \times 1$ matrix of simple sphalerite cells in which the cationic and anionic sites are both substituted by Cu, As and S. These three atoms are represented in the same way as in Fig. 1.

* Reflexions 310, 600 and 002 were omitted from this calculation as they were considered to suffer from extinction.

As_4S_4 (2.54(10) Å), and gaseous As_4 (2.44(3) Å). The chains are perfectly planar and the included As-As-As angle is 97.7(1)°. Arsenic atoms in the chain complete a tetrahedral environment by covalent bonding with a copper and a sulphur atom.

The tetrahedral distribution of bonds about arsenic is not as common in minerals as the trigonal-pyramidal distribution. Thus, for example, in scleroclase, PbAs_2S_4 (Nowacki, Iitaka, Burki & Kunz, 1961), (Iitaka & Nowacki, 1961), seligmannite, CuPbAsS_3 (Hellner & Leineweber, 1956), gratonite, $9\text{PbS} \cdot 2\text{As}_2\text{S}_3$ (Rösch, 1963), baumhauerite, $\text{Pb}_5\text{As}_9\text{S}_{18}$ (Le Bihan, 1961), rathite I, II and III (Le Bihan, 1962), and dufrenoyite (Nowacki, Bahezre & Marumo, 1963) the arsenic atoms are surrounded by a trigonal pyramid of sulphur atoms which then share corners to form infinite strings of polyhedra.

Discussion

Sphalerite, or $\beta\text{-ZnS}$, has a face centred cubic type structure with four zinc atoms at 0,0,0 *etc.* and sulphur atoms at $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ *etc.* Each atom has about it four equally distant atoms of the opposite sort arranged at the corners of a regular tetrahedron. Two types of derivative structure have previously been reported:

(a) Complex derivatives such as chalcopyrite $\text{Cu}_2\text{Fe}_2\text{S}_4$, luzonite Cu_3AsS_4 , famatinite Cu_3SbS_4 and germanite $\text{Cu}_3(\text{Fe},\text{Ge})\text{S}_4$ in which the cationic sites contain atoms other than zinc and each metal atom is surrounded by a tetrahedron of sulphur atoms. The metal to sulphur ratio remains unchanged at 1:1.

(b) Complex-defect derivatives such as tetrahedrite $(\text{Cu},\text{Ag},\text{Fe})_{12}\text{Sb}_4\text{S}_{13}$ and tennantite $(\text{Cu},\text{Ag},\text{Fe})_{12}\text{As}_4\text{S}_{13}$ in which some of the sulphur positions are vacant. The cationic zinc sites are again substituted by other metal atoms; those other than As or Sb have a tetrahedral environment, but the As and Sb atoms exhibit their more common trigonal pyramidal configuration. The ratio of metal to sulphur atoms is thus greater than one.

Lautite does not appear to resemble any of the above complex-derivative structures. It can be derived from the sphalerite structure by taking a large unit of $3 \times 3 \times 1$ cubic sphalerite cells (Fig. 2) and substituting not only the zinc cationic positions as above, but also the anionic sulphur positions. The zinc sites are occupied by Cu ($\frac{1}{3}$), As ($\frac{1}{3}$) and S ($\frac{1}{3}$), whilst the sulphur sites are also occupied by Cu ($\frac{1}{3}$), As ($\frac{1}{3}$) and S ($\frac{1}{3}$). The structure is perfectly ordered and may perhaps be better compared to a substituted diamond lattice where no distinction is made between metal and non-metal atomic sites.

The vectors of the simple sphalerite unit cell (1) are related to the vectors of the lautite unit cell (2) by the index transform –

$$\begin{array}{c} \rightarrow 1 \\ \downarrow 2 \\ \boxed{\begin{array}{ccc} 0 & \frac{1}{3} & -\frac{1}{3} \\ 1 & 0 & 0 \\ 0 & 1 & 1 \end{array}} \end{array}$$

Note added in proof. – The structure of lautite, refined in the space group $Pnam$, has recently been reported by Marumo & Nowacki (1964). Their data can be better fitted to the structure based upon the space group $Pna2$, and a note to this effect is forthcoming.

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