Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Reinvestigation of the crystal structure of lautite, CuAsS

Luca Bindi,[a] Tiziano Catelani,[b] Laura Chelazzi[b] and Paola Bonazzi[b]*

[a]Museo di Storia Naturale, Sezione di Mineralogia, Universitá degli Studi di Firenze, Via La Pira 4, I-50121 Firenze, Italy, and [b]Dipartimento di Scienze della Terra, Universitá degli Studi di Firenze, Via La Pira 4, I-50121 Firenze, Italy
Correspondence e-mail: pbcry@geo.unifi.it

Received 25 January 2008; accepted 14 February 2008

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(As–S) = 0.002 Å; R factor = 0.046; wR factor = 0.109; data-to-parameter ratio = 30.2.

The crystal structure of the mineral lautite (copper arsenic sulfide), CuAsS, previously described as either centrosymmetric [*Pnma*; Marumo & Nowacki (1964). *Schweiz. Miner. Petro. Mitt.* **44**, 439–454] or noncentrosymmetric [$Pna2_1$; Craig & Stephenson (1965). *Acta Cryst.* **19**, 543–547], was reinvestigated by means of single-crystal X-ray diffraction. The centrosymmetric structural model reported previously was confirmed, although with improved precision for the atomic coordinates and interatomic distances. Lautite shows a sphalerite-derivative structure with a linking of $Cu[AsS_3]$, $As[CuAs_2S]$ and $S[Cu_3As]$ tetrahedra. All atoms lie on special positions (Wyckoff position 4*c*, site symmetry *m*).

Related literature

For related literature, see: Craig & Stephenson (1965); Marumo & Nowacki (1964); Wyckoff (1963).

Experimental

Crystal data

AsCuS
M_r = 170.54
Orthorhombic, *Pnma*
a = 11.347 (4) Å
b = 3.7533 (7) Å
c = 5.453 (1) Å
V = 232.24 (10) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 24.00 mm^{-1}
T = 298 (2) K
0.12 × 0.10 × 0.08 mm

Data collection

Bruker *P*4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.070, T_{max} = 0.150
3824 measured reflections
574 independent reflections
483 reflections with $I > 2\sigma(I)$
R_{int} = 0.077
3 standard reflections
every 150 reflections
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.108
S = 1.09
574 reflections
19 parameters
$\Delta\rho_{max}$ = 1.28 e Å^{-3}
$\Delta\rho_{min}$ = −1.07 e Å^{-3}

Data collection: *XSCANS* (Bruker, 1997); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *Xtal-draw* (Downs & Hall-Wallace, 2003); software used to prepare material for publication: *SHELXL97*.

This work was funded by CNR, Istituto di Geoscienze e Georisorse, Sezione di Firenze.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FI2059).

References

Bruker (1997). *XSCANS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Craig, D. C. & Stephenson, N. C. (1965). *Acta Cryst.* **19**, 543–547.
Downs, R. T. & Hall-Wallace, M. (2003). *Am. Mineral.* **88**, 247–250.
Marumo, F. & Nowacki, W. (1964). *Schweiz. Miner. Petro. Mitt.* **44**, 439–454.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Wyckoff, R. W. G. (1963). *Crystal Structures*, 2nd ed. New York: Interscience Publishers.

supplementary materials

Acta Cryst. (2008). E**64**, i22 [**doi:10.1107/S1600536808004492**]

Reinvestigation of the crystal structure of lautite, CuAsS

L. Bindi, T. Catelani, L. Chelazzi and P. Bonazzi

Comment

The crystal structure of lautite was solved by Marumo & Nowacki (1964) in the space group *Pnma* (R = 9.0%) and by Craig & Stephenson (1965) in the space group $Pna2_1$ (R = 13.7%) by means of photographic data and three-dimensional Patterson-function. The low quality of the structural data given by these authors, however, did not allow to obtain an anisotropic model of the structure. Nevertheless, the topologies and interatomic distances of both centrosymmetric and non-centrosymmetric models are very similar.

Although the structural results obtained by Craig & Stephenson (1965) indicate the acentricity of the structure of CuAsS, no clear crystal-chemical reason for the choice of a noncentrosymmetric arrangement was given. To help resolve the concerns relating to the structure of natural lautite, we present new crystal structure data for lautite from its type locality (*i.e.*, Marienberg, Saxony, Germany).

The centrosymmetric structural model previously reported by Marumo & Nowacki (1964) was confirmed, although a higher precision of refinement was achieved (e.s.d. improved by a factor of two) and refinement with anisotropic displacement parameters could be performed (Fig. 1). All atoms lie on special positions (Wyckoff position 4c, site symmetry m). Lautite shows a sphalerite-derivative structure with a linking of $Cu[AsS_3]$, $As[CuAs_2S]$ and $S[Cu_3As]$ tetrahedra (Fig. 2). Within the framework, the As atoms form zigzag As—As chains along [010] exhibiting As—As bond distances [2.4965 (8) Å] and angles [97.48 (4)°] resembling the covalent As—As linkage observed within the sheets of the crystal structure of arsenic (Wyckoff, 1963).

Experimental

A crystal was selected from a natural specimen belonging to the Mineralogical Collection of the Natural History Museum of Florence (catalogue number 44202/G).

Refinement

The crystal structure refinement was performed starting from the atomic coordinates reported by Marumo & Nowacki (1964). Convergence was rapidly obtained for an anisotropic model of the structure.

Figures

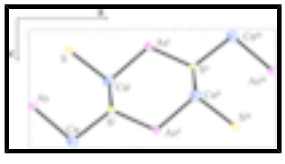

Fig. 1. The crystal structure of lautite down [010]. Displacement parameters are drawn at the 70% probability level. The unit-cell is outlined. Symmetry codes are: (i) $-x + 1/2$; $-y$; $z + 1/2$; (ii) $x + 1/2$; $-y + 1/2$; $-z + 1/2$; (iii) $-x$; $y + 1/2$; $-z$.

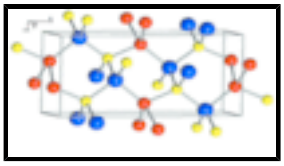

Fig. 2. The crystal structure of lautite showing the linking of Cu[AsS_3], As[$CuAs_2S$] and S[Cu_3As] tetrahedra. Blu, red and yellow circles indicate Cu, As and S atoms, respectively. The unit-cell is outlined.

copper arsenic sulfide

Crystal data

AsCuS	F_{000} = 312
M_r = 170.54	D_x = 4.878 Mg m^{-3}
Orthorhombic, *Pnma*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P 2ac 2n	Cell parameters from 38 reflections
a = 11.347 (4) Å	θ = 12.5–24.3°
b = 3.7533 (7) Å	μ = 24.00 mm^{-1}
c = 5.453 (1) Å	*T* = 298 (2) K
V = 232.24 (10) Å^3	Block, black
Z = 4	0.12 × 0.10 × 0.08 mm

Data collection

Bruker P4 diffractometer	R_{int} = 0.077
Radiation source: fine-focus sealed tube	θ_{max} = 35.0°
Monochromator: graphite	θ_{min} = 3.6°
T = 298(2) K	*h* = −18→18
ω scans	*k* = −6→6
Absorption correction: ψ scan (North *et al.*, 1968)	*l* = −8→8
T_{min} = 0.070, T_{max} = 0.150	3 standard reflections
3824 measured reflections	every 150 reflections
574 independent reflections	intensity decay: none
483 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.046	$w = 1/[\sigma^2(F_o^2) + (0.0856P)^2 + 1.9844P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.108	$(\Delta/\sigma)_{max} < 0.001$
S = 1.09	$\Delta\rho_{max}$ = 1.28at 0.0736 0.2500 0.3457 (0.68 Å from As) e Å^{-3}
574 reflections	$\Delta\rho_{min}$ = −1.07at 0.0052 0.0883 0.4402 (0.78 Å from As) e Å^{-3}

19 parameters Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu	0.17454 (7)	0.2500	0.06264 (18)	0.0165 (2)
As	0.01373 (5)	0.2500	0.35177 (11)	0.00894 (18)
S	0.16576 (12)	0.7500	0.8196 (3)	0.0100 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu	0.0171 (3)	0.0168 (4)	0.0157 (4)	0.000	−0.0015 (3)	0.000
As	0.0105 (3)	0.0084 (3)	0.0080 (3)	0.000	0.00083 (17)	0.000
S	0.0108 (5)	0.0114 (5)	0.0079 (5)	0.000	−0.0005 (4)	0.000

Geometric parameters (Å, °)

Cu—S^{i}	2.2908 (16)	As—As^{v}	2.4965 (8)
Cu—S^{ii}	2.2996 (10)	S—As^{iv}	2.2408 (16)
Cu—S^{iii}	2.2996 (10)	S—Cu^{vi}	2.2908 (16)
Cu—As	2.4114 (11)	S—Cu^{vii}	2.2996 (10)
As—S^{iv}	2.2408 (16)	S—Cu^{viii}	2.2996 (10)
As—As^{iv}	2.4965 (8)		
S^{i}—Cu—S^{ii}	112.76 (3)	S^{iv}—As—As^{v}	99.01 (4)
S^{i}—Cu—S^{iii}	112.76 (3)	Cu—As—As^{v}	121.19 (3)
S^{ii}—Cu—S^{iii}	109.39 (7)	As^{iv}—As—As^{v}	97.48 (4)
S^{i}—Cu—As	101.46 (5)	As^{iv}—S—Cu^{vi}	117.64 (7)
S^{ii}—Cu—As	110.12 (4)	As^{iv}—S—Cu^{vii}	106.24 (5)
S^{iii}—Cu—As	110.12 (4)	Cu^{vi}—S—Cu^{vii}	108.56 (4)
S^{iv}—As—Cu	114.52 (5)	As^{iv}—S—Cu^{viii}	106.24 (5)
S^{iv}—As—As^{iv}	99.01 (4)	Cu^{vi}—S—Cu^{viii}	108.56 (4)
Cu—As—As^{iv}	121.19 (3)	Cu^{vii}—S—Cu^{viii}	109.39 (7)

Symmetry codes: (i) −*x*+1/2, −*y*+1, *z*−1/2; (ii) *x*, *y*−1, *z*−1; (iii) *x*, *y*, *z*−1; (iv) −*x*, −*y*+1, −*z*+1; (v) −*x*, −*y*, −*z*+1; (vi) −*x*+1/2, −*y*+1, *z*+1/2; (vii) *x*, *y*+1, *z*+1; (viii) *x*, *y*, *z*+1.

Fig. 1

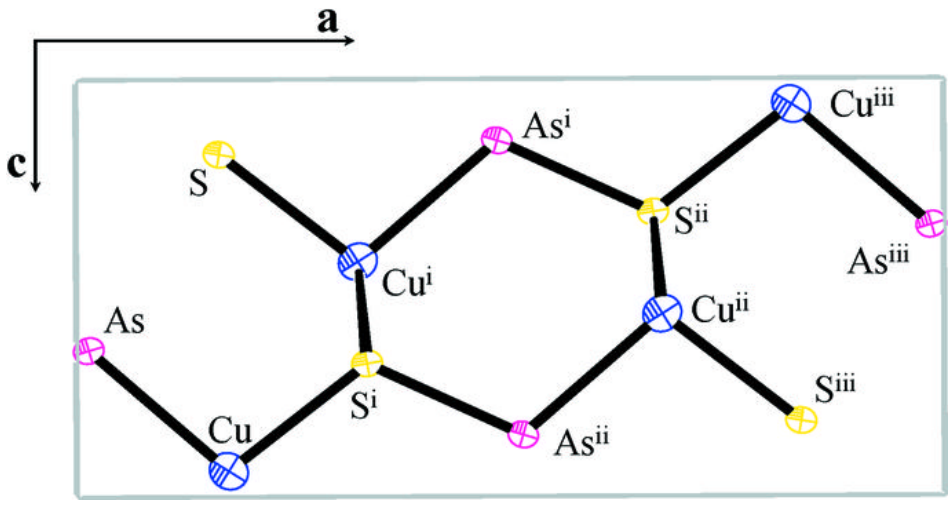

Fig. 2