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Stalderite $\text{TlCu}(\text{Zn},\text{Fe},\text{Hg})_2\text{As}_2\text{S}_6$ – a new mineral related to routhierite: description and crystal structure determination

Dedicated to Prof. Hans A. Stalder, on occasion of his 70th birthday

by Stefan Graeser^{1,2}, Hans Schwander², Reinhard Wulf³ and Andreas Edenthaler⁴

Abstract

A new Tl-sulfosalt mineral, stalderite $\text{TlCu}(\text{Zn},\text{Fe},\text{Hg})_2\text{As}_2\text{S}_6$, was found in small cavities of hydrothermal origin in a Triassic dolomite at the famous sulfosalt locality Lengenbach, Binntal (Ct. Valais, Switzerland). The black coloured mineral occurs in well shaped isometric crystals (< 1 mm) in close association with various other Tl- and As-rich minerals such as: hutchinsonite, hatchite, wallisite, edenharderite, bernardite, besides abundant realgar and orpiment. Single-crystal X-ray studies yielded a tetragonal cell with $a = 9.855$ (3) Å, $c = 10.937$ (7) Å, $Z = 4$. The six strongest lines in the X-ray powder diagram are (d_{obs} in Å, I_{obs} , hkl): 2.940 (100)(222), 4.086 (51)(211), 2.436 (39)(303), 3.417 (34)(103), 1.743 (23)(440), 1.806 (22)(521). Chemical composition (electron microprobe, mean of three analyses, weight%) is: Tl 25.80, Cu 7.20, Ag 0.23, Pb 2.25, Zn 9.16, Fe 3.02, Hg 8.90, As 18.48, S 24.48, total 99.52%. From X-ray and chemical data, the close relationship with the mineral routhierite TiHgAsS_3 , of which stalderite represents the Zn-equivalent, was easily recognizable. Stalderite crystals are opaque black with a characteristic red and blue tarnish; the streak is brown-red. The fracture is uneven to conchoidal; no cleavage could be observed. The microhardness VHN (10 g load) is 135 (132–138) kg/mm², corresponding to a Mohs hardness of 3½–4. The calculated density $D_{\text{calc}} = 4.97$ g/cm³; the direct density could not be determined because of small grain size.

The structure determination was carried out using data from single-crystal measurements with synchrotron radiation ($\lambda = 1.1213$ Å) on the 4-circle diffractometer (Huber) at HASYLAB, Hamburg. The space group is $I\bar{4}2m$ with $a = 9.865$ (1) Å, $c = 10.938$ (2) Å, $Z = 4$. The structure was solved by an Automated Patterson Interpretation (SHELXS 92) using all 358 unique reflections and refined (SHELXL 92) with anisotropic temperature factors to an R-value of 0.047.

The Tl atom is coordinated by (2 + 4)S atoms in form of an orthorhombic pyramid with a split apex (mean Tl–S = 3.32 Å). The Cu as well as the (Zn,Fe,Hg) atoms are surrounded by four S atoms. The polyhedra are slightly distorted tetrahedra (mean Cu–S = 2.36 Å, mean (Zn,Fe,Hg)–S = 2.41 Å). The As atom forms a trigonal pyramid with three S atoms, with the As atom at the apex (mean As–S = 2.30 Å).

The structure of stalderite is characterized by a three-dimensional network of the CuS_4 - and $(\text{Zn},\text{Fe},\text{Hg})\text{S}_4$ -tetrahedra. This network shows channels along the c-axis, where the Tl- and the As-atoms are located at the positions (0,0,z) and (x,x,z), respectively. Whereas the Tl–As distance of 3.48 Å is quite usual for Tl–As sulfosalts, the Tl–Tl distance of 3.29 Å is remarkably short, indicating a tendency of Tl–Tl interactions. The structure determinations of stalderite and of routhierite confirm the close relationship of both minerals.

Keywords: stalderite, new mineral, Tl–Pb–Zn–As-sulfosalt, microprobe analyses, synchrotron radiation, structure determination, Lengenbach, Switzerland.

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1. Introduction

Within the last hundred years, the famous sulfosalt locality Lengenbach in Binntal (Ct. Valais, Switzerland) has provided the systematic mineralogy with a remarkable number of new sulfosalt species, of mainly Pb–As–S composition. The classical old site where minerals had been exploited for scientific purpose since at least the early 19th century had to be abandoned in 1986 for technical reasons but also because of the increasingly unattractive mineral content. During the summer months in 1987, a new quarry was opened about 25–30 meters above the working level in the old site and some 30–40 meters farther to the east. The decision to move to this new site was influenced by the detection of three new thallium-sulfosalts found in a loose block that fell from the new area into the old quarry in 1985. These new minerals were: edenharderite $\text{TlPbAs}_3\text{S}_6$ (GRAESER and SCHWANDER, 1992), ernigglite $\text{Tl}_2\text{SnAs}_2\text{S}_6$ (GRAESER et al., 1992), and the mineral stalderite described in the present paper (L 18'581 from the official exploitation).

Since 1988, the new site in Lengenbach has been operating with remarkable success and has produced a large number of interesting minerals. At least one additional new Tl-sulfosalt was found that was accepted under the name jentschite ($\text{TlPbAs}_2\text{Sb}_1\text{S}_6$) by the Commission on New Minerals and Mineral Names, I.M.A. (GRAESER et al., in preparation). An additional unknown Tl–Cu–Ag–As–S mineral is still under investigation. Almost simultaneously with the first description of bernardite $\text{Tl}(\text{As},\text{Sb})_5\text{S}_8$ (PASAVA et al., 1989), this mineral was also found in Lengenbach (1989).

The name is for Prof.(emeritus) Dr. Hans A. Stalder (*1925), former head of the mineralogy department, Natural History Museum of Berne who for many years served as a secretary of the "Arbeitsgemeinschaft Lengenbach".

Type specimens are preserved at the Natural History Museum and Mineralogical Institute, University of Basel. Name and mineral data were approved by the Commission on New Minerals and Mineral Names, I.M.A., prior to the publication.

The mineral and name stalderite was accepted by the Commission on New Minerals and Mineral Names, I.M.A. in 1987. Already from preliminary investigations it became obvious that the mineral is closely related to the mineral routhierite, described by JOHAN et al. (1974), of which stalderite represents the Zn-dominant equivalent. Because of unfortunate circumstances the publication of the mineral stalderite was strongly delayed.

2. Physical and optical properties

The unknown mineral was detected when looking through the material extracted from the dolomitic rock by Toni Imhof and his team on behalf of the Lengenbach syndicate ("Arbeitsgemeinschaft Lengenbach"). We were attracted by the uncommon morphology of the mineral; the first visual inspection under the binocular lead to a misinterpretation of the crystal symmetry: it was considered to be cubic with cuboctahedral shape. The error is easily understood if the SEM picture of the original crystal (Fig. 1) is rotated about 90° in anti-clockwise sense, the mineral unmistakably reminds of a cubic crystal. Practically all the preliminary studies were carried out on this almost perfectly shaped crystal (of 0.4 mm in diameter). A single-crystal Gandolfi diagram clearly proved that the mineral was not identical with any Lengenbach sulfosalt known so far.

Stalderite, like all the numerous other Lengenbach sulfosalt minerals, occurs in small cavities of hydrothermal origin in the Triassic dolomite (druses). On the few samples known so far containing stalderite, the mineral always forms euhedral, isometric crystals that strongly resemble a cubic mineral, their maximum size does not exceed 0.5 mm. Stalderite crystals display a very characteristic black colour with metallic lustre, a slight blue and red tarnish seems to be very typical for the mineral. Stalderite is completely opaque, with a Mohs hardness of about $3\frac{1}{2}$ –4 (corresponding to a microhardness of $\text{VHN} = 135 \text{ kg/mm}^2$); it is brittle and shows no indication of cleavage. Like ernigglite, stalderite is an ex-

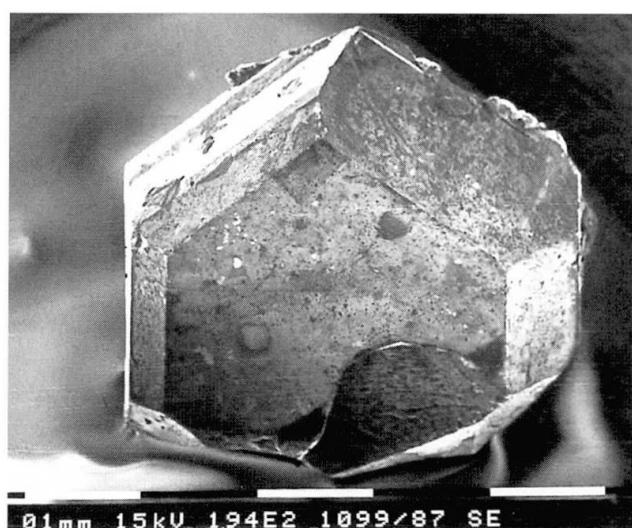


Fig. 1 SEM picture of stalderite. The crystal habit is dominated by the strong development of the prism {110} and the dipyramid {101} (Picture: SEM laboratory, University of Basel).

Tab. 1 Physical and optical properties of stalderite.

Morphology	isometric, pseudocubic
Forms	prisms {110} and {100} tetragonal dipyramid {101} ditetragonal bipyramids {213}, {211}
Colour	black, with slight blue and red tarnish
Streak	brown-red
Hardness	VHN _{10g} = 135 kg/mm ² (132–138) → MOHS = 3.5–4
Cleavage	not observed
Fracture	uneven, brittle
Density:	4.97 g/cm ³ (calculated)
Ore microscopy (LEITZ MPV-compact microscope)	
Colour	greyish white
Internal reflections	rarely in reds
Bireflectance	none observed
Anisotropism	very weak
Reflectance values	(WTiC standard, air) minimum-maximum values 480 nm 27.0–30.5% 546 nm 27.0–28.0% 589 nm 25.0–27.0% 656 nm 24.4–25.5%

tremely rare species, known in about ten samples so far – in contrast to the closely associated edenharterite, from which more than 100 specimens have been identified within the past eight years.

In polished section under reflected light, stalderite displays a greyish-white colour, with rare deep red internal reflections. Anisotropy is very weak, bireflectance or pleochroism could not be observed. Reflectance values (see Tab. 1) are moderate and extremely close to other Tl-sulfosalts such as ernigglite (GRAESER et al., 1992), edenharterite (GRAESER and SCHWANDER, 1992), hutchinsonite (GRAESER, 1965) from Lengenbach.

The same crystal, as used for X-ray single-crystal investigation, was measured on an optical goniometer (Terpstra) for identification of the crystal faces. The size of the crystal (0.4 mm across) was practically beyond the feasibility of the goniometer; the main difficulty was to attribute the reflection signals to the proper corresponding crystal faces. The crystal habit is defined by the development of a large prism {110} and dipyramid {101}, additional forms are {100}, {121} and {112} (see Tab. 2, Fig. 2). The c/a ratio determined from the position of the faces {101} and {112} agrees excellently with the one calculated from the cell parameters, 1.109 and 1.1098, respectively.

Tab. 2 Stalderite, measurements on optical goniometer.

Forms	φ_{obs}	ρ_{obs}	φ_{calc}	ρ_{calc}
1 0 0	90°	90°	90°	90°
1 1 0	45°	90°	45°	90°
1 0 1	90°	47.9°	90°	47.98°
1 1 2	45°	38.2°	45°	38.13°
1 2 1	26.6°	66.4°	26.5°	68.06°
c/a = 1.109 (calculated from {101} and {112} faces)				

3. Chemical composition

The unknown mineral consequently was investigated by SEM techniques (Cambridge Stereoscanner Mark 2A, equipped with EDS analytical system, University of Basel) with respect to its morphology and qualitative chemical composition. From the EDS analysis the following elements were detected: Ti, Cu, Zn, Fe, As, S – the element Hg was not yet found. The next step was to carry out a quantitative microprobe analysis. Meanwhile it became obvious from single-crystal data that the mineral is closely related to rou-

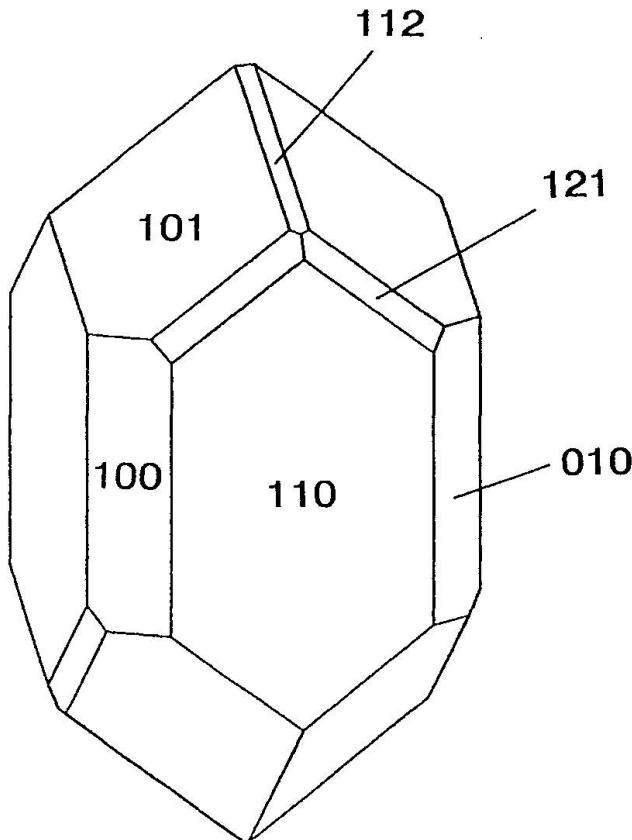


Fig. 2 Stalderite, idealized crystal drawing (SHAPE) according to measurements on an optical goniometer.

Tab. 3 Microprobe analyses of stalderite from Lengenbach (wt%).

	A	B	C	D	E
Tl	24.91	25.78	26.70	25.80	25.86
Cu	7.35	7.33	6.90	7.20	8.04
Ag	0.19	.08	0.39	0.23	
Pb	1.85	2.65	—	2.25	
Zn	10.10	9.05	8.32	9.16	9.10
Fe	2.11	3.13	3.82	3.02	3.53
Hg	9.69	8.56	8.45	8.90	10.15
As	18.13	17.67	19.65	18.48	18.96
S	24.65	24.52	24.27	24.48	24.36
Total	98.98	98.77	98.50	99.52	100.00
Structural formula (based on 12 atoms):					
Tl	.98	1.02	1.04	1.02	1.0
Cu	.94	.94	.88	.91	1.0
Zn	1.25	1.12	1.02	1.13	1.1
Fe	.30	.45	.55	.44	0.5
Hg	.39	.35	.34	.36	0.4
As	1.95	1.91	2.10	1.99	2.0
S	6.19	6.20	6.06	6.16	6.0

A, B, C analyses of individual crystals

D mean of three analyses

E composition for $TlCu(Zn_{1.1}Fe_{.5}Hg_{.4})As_2S_6$

thierite $TlHgAsS_3$ described by JOHAN et al. (1974), therefore the element Hg was tested in particular. The analyses were carried out on an ARL instrument (SEMQ, TN 2000, ZAF program), the following standard materials were used: synth. $TlAsS_2$ (Tl, As, S), galena (Pb), cinnabarite (Hg), and pure elements (Pb, Zn, Cu, Fe, Ag). Three individual analyses of different crystal fragments lead unequivocally to the following formula: $TlCu(Zn,Fe,Hg)_2As_2S_6$ (see Tab. 3.). The fact that the Tl and Cu contents in atomic numbers are close to 1:1 suggested different sites for the two elements, an assumption that was subsequently proven by the structure determination.

4. X-ray diffraction study

Preliminary X-ray powder data were obtained from the whole single crystal of 0.4 mm (Fig. 1) by the Gandolfi X-ray camera. The diagram could not be identified with any known mineral nor could additional powder diagrams, obtained by common Debye-Scherrer cameras. The subsequent single-crystal study (Weissenberg and Precession techniques) lead to a tetragonal mineral with a body-centered cell, Laue group I4/mmm.

As the number of sulfosalt minerals with tetragonal symmetry is quite restricted, it was easy to state the relationship with the Tl-Hg-As-sulfosalt routhierite. In combination with the chemical data, the unknown mineral turned out to be a new sulfosalt species – the Zn-equivalent of routhierite in which most of the mercury was substituted by zinc. Powder diffraction data are given in table 4.

Since the first discovery of the mineral only about ten stalderite samples have been detected, all of them were identified by X-ray diffraction. The d-values obtained from these samples showed some variation, and the refinement of lattice parameters from the powder data indicated that especially the c parameter is subject to variations: $a = 9.855\text{--}9.868$ (3) Å, $c = 10.937\text{--}11.064$ (4) Å. This variation in lattice parameters is undoubtedly caused by chemical variations in the (Zn,Fe,Hg)-site.

5. Occurrence

Stalderite is a member of numerous Pb-Cu-Tl-Ag-As-sulfosalt minerals occurring in rounded cavities (druses) of the Triassic dolomite at the lo-

Tab. 4 X-ray diffraction data for stalderite.

h	k	l	d_{calc}	d_{obs}	I/I_1
1	1	0	6.97	6.91	5
2	0	0	4.928	4.932	5
2	1	1	4.088	4.086	51
2	0	2	3.661	3.666	5
1	0	3	3.419	3.417	34
3	1	0	3.116	3.116	14
2	2	2	2.938	2.940	100
2	1	3	2.809	2.820	6
3	1	2	2.708	2.693	6
3	2	1	2.652	2.651	15
1	1	4	2.545	2.541	20
3	0	3	2.440	2.436	39
2	0	4	2.391	2.393	10
4	1	1	2.335	2.326	9
3	3	0	2.323		
3	1	4	2.055	2.055	10
4	1	3	1.9988	1.9984	15
4	0	4	1.8303	1.8311	15
5	2	1	1.8049	1.8060	22
4	4	0	1.7421	1.7431	23
4	2	4	1.7157	1.7141	12
6	1	1	1.6026	1.6046	9
6	0	2	1.5730	1.5722	12
6	2	2	1.4985	1.4983	14
				1.4867	6
				1.4421	6
				1.4122	5
				1.1609	7

 $a = 9.855 (3) \text{ \AA}$ $c = 10.937 (7) \text{ \AA}$ $V = 1062.3 (7) \text{ \AA}^3$ $c/a = 1.1098$

Debye-Scherrer camera, 114.6 mm diameter, FeK_α -radiation, intensities determined densitometrically. Cell parameters refined from powder data.

cality Lengenbach in Binntal, Ct. Valais, Switzerland. All these minerals presumably were formed by the activity of Tl-As-bearing hydrothermal solutions during Alpine metamorphism. Most of the sulfosalts, stalderite in particular, occur in idiomorphic crystals of small size, rarely exceeding 1–2 mm. On the few samples containing stalderite so far, the mineral is closely associated with other Tl-As-rich minerals such as hutchinsonite, hatchite, realgar, orpiment. Its occurrence seems to be strictly limited to the new working level of the Lengenbach quarry about 25 meters above the bottom of the old classical location on the righthand bank of the Lengenbach stream. A more detailed description of the old and new sites is given in GRAESER (1965) and GRAESER and SCHWANDER (1992a).

When the "Arbeitsgemeinschaft Lengenbach", the syndicate exploiting the Lengenbach

Tab. 5 Tl-minerals in Lengenbach (in chronological order).

*hatchite	$\text{TiPbAgAs}_2\text{S}_5$	1902	1)
*hutchinsonite	$\text{TiPbAs}_5\text{S}_9$	1903	2)
*wallsite	$\text{TiPbCuAs}_2\text{S}_5$	1963	3)
*imhofite	$\text{Ti}_6\text{As}_{15}\text{S}_{25}$	1964	4)
lorandite	TiAsS_2	1966	5)
*edenharterite	$\text{TiPbAs}_3\text{S}_6$	1985	6)
*erniggliite	$\text{Ti}_2\text{SnAs}_2\text{S}_6$	1985	7)
*stalderite	$\text{TiCu}(\text{Zn},\text{Fe},\text{Hg})_2\text{As}_2\text{S}_6$	1985	8)
bernardite	$\text{Ti}(\text{As},\text{Sb})_5\text{S}_8$	1990	9)
*jentschite	$\text{TiPbAs}_2\text{Sb}_1\text{S}_6$	1990	10)
(unknown:	Tl-Pb-Cu-Ag-As-S phase	1988	

1) SALLY and SMITH (1912), NOWACKI et al. (1964); 2) SALLY (1905); 3) NOWACKI (1965); 4) BURRI et al. (1965); 5) GRAESER (1967); 6) GRAESER and SCHWANDER (1992a); 7) GRAESER et al. (1992); 8) this paper; 9) GRAESER, in HOFMANN et al. (1992); 10) GRAESER et al. (1995).

* = first description (type locality Lengenbach)

minerals since 1958, opened the new site in 1988, a most striking feature was detected concerning the chemical composition of the minerals from this site: they display much higher contents of the elements Tl and As than those from the classical locality. Whereas Tl-As-sulfosalts (hutchinsonite, hatchite) from here represented extreme rarities in the past, the same minerals and additional members were found in numerous samples at the new site. The mineral hatchite e.g., described by SALLY and SMITH (1912) – only crystallographic data, a chemical determination was not possible because of lack of material – existed until 1964 only in a few extremely small crystals. The chemical nature as of a Tl-mineral was determined by microprobe technique on new material found in 1963 (NOWACKI et al., 1964). Within a short period, more hatchite material was found at the new site than in the 80 years since the mineral was first described. Moreover, hutchinsonite became a very common mineral and several new species could be determined (Tab. 5).

Another Lengenbach mineral, rathite ($\text{Pb}, \text{Ti})_3\text{As}_5\text{S}_{10}$, figuring within most compilations of Tl-As-sulfosalts (NOWACKI und BAHEZRE, 1963) should not be considered as a genuine Tl-mineral according to our knowledge. Most Pb-Cu-As-sulfosalts like sartorite, dufrénoysite, tennantite ("binnite"), etc. from the new site contain considerable amounts of Tl and therefore change their colour from black into red (translucent in thin fragments). Yet, all these minerals may exist without any Tl-content, and do not represent Tl-minerals in the real sense. Despite this restriction,

Tab. 6 Fractional atomic coordinates and isotropic thermal parameters U_{equ} of stalderite, $\text{TlCu}(\text{Zn},\text{Fe},\text{Hg})_2\text{As}_2\text{S}_6$ from synchrotron data ($\lambda = 1.1213 \text{ \AA}$).

	x	y	z	$U_{\text{equ}} [\text{\AA}^2]$
Tl	0.0	0.0	0.3501(2)	0.0453(6)
Cu	0.0	0.5	0.25	0.0096(8)
Zn, Fe, Hg	0.2253(2)	0.5	0.5	0.0183(5)
As	0.2628(2)	0.2628(2)	0.2495(6)	0.0177(7)
S(1)	0.1010(4)	0.3385(4)	0.3801(4)	0.0148(9)
S(2)	0.1265(4)	0.1265(4)	0.1330(5)	0.0143(12)

with the minerals from the new site the Lengenbach occurrence has advanced to one of the most prominent Tl-mineralisations worldwide, with almost half of all known Tl-minerals occurring at this locality. The study of an additional unknown Tl-Pb-Cu-Ag-As-phase could not be accomplished by now because no adequate material was available for single-crystal work (only in multiple twins).

6. Experimental

6.1. THE USE OF SYNCHROTRON RADIATION

Synchrotron radiation may be roughly described as a pulsed and highly polarized "white radiation" of high brilliance (i.e. high intensity and high collimation) over a wide spectral range up to the hard X-ray wave lengths. Depending on the spectral range used for the experiments, specific monochromators are designed to select the appropriate wavelength from the "white spectrum". In the case of measurements using the X-ray range so called "fixed exit monochromators" based on a two-fold Bragg-reflection on two independent single crystals, usually Ge(111) or Si(111), are at present "state of the art" (KUPCIK et al., 1983 and 1986). The main advantages of using synchrotron radiation in single crystal work

have already been summarized in a short overview on the structure of ernigglite $\text{TiSnAs}_2\text{S}_6$ (GRAESER et al., 1992).

6.2. MEASURING PROCEDURE, DATA COLLECTION AND DATA REDUCTION

Single crystal measurements on stalderite were carried out on the 4-circle diffractometer at HASYLAB (Hamburger Synchrotron Labor) at DESY (Deutsches Elektronen-Synchrotron). The use of synchrotron radiation was necessary since only very small crystals were available. The dimensions of the best crystal, selected for the single crystal measurements, were $0.048 \times 0.024 \times 0.016 \text{ mm}$. Using a 4-circle diffractometer attached to a conventional X-ray tube (Mo-K α , 1.5 kW, graphite monochromator) only few reflections were measured. The wavelength used (1.1213 \AA) was selected as a compromise between a) high scattering power, b) high photon flux and c) the necessity of avoiding the closeness of an absorption edge. From 38 reflections in the range of $22.0\text{--}54.1^\circ 2\Theta$ the lattice parameters were determined by least square refinement to be $a = 9.865 (4) \text{ \AA}$, $c = 10.938 (5) \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$. With $Z = 4$, the calculated density is $\rho = 4.95 \text{ g/cm}^3$. These results are in good agreement with those obtained from powder diffraction

Tab. 7 Interatomic distances (\AA) in stalderite (standard deviations in brackets).

Tl	-	S(2)	2.959(6)	2×	Cu	-	S(1)	2.357(4)	4×
	-	S(1)	3.500(5)	4×					
mean Tl - S			3.320						
Tl	-	Tl	3.279(4)						
Tl	-	As	3.484(5)	4×					
Zn*	-	S(1)	2.401(4)	2×	As	-	S(1)	2.269(6)	2×
	-	S(2)	2.410(4)	2×		-	S(2)	2.289(7)	
mean Zn - S			2.406		mean As - S			2.297	

* with minor contents of Fe, Hg

measurements. The data collection was carried out using a special measuring procedure (WENDSCHUH-JOSTIES and WULF, 1989), developed especially for single crystal diffraction experiments with synchrotron radiation. The reflection profiles indicate that the crystal used was of relatively poor quality, due to the peak width (FWHM) varying from $0.08\text{--}0.28^\circ 2\Theta$. The latter value is rather large for synchrotron radiation and points to an extended mosaic spread of the crystal. Moreover, the profiles were partially split or showed an asymmetric shape depending on the crystallographic direction. In terms of counting the crystal size was optimal: the maximal

count rate was about 20'000 cps, high enough to obtain a good counting statistic. Since the dead time correction is valid up to this counting rate no attenuation filters – a general source of systematic errors – were necessary.

Using the synchrotron data reduction program SYNRED (WENDSCHUH-JOSTIES and WULF, unpublished) the raw intensity data were corrected for deadtime loss, scaled by the monitor intensities and finally corrected for Lorentz- and polarization-effects. A semi-empirically absorption correction was applied using the psi-scan technique (XEMP, SHELDRICK, 1976).

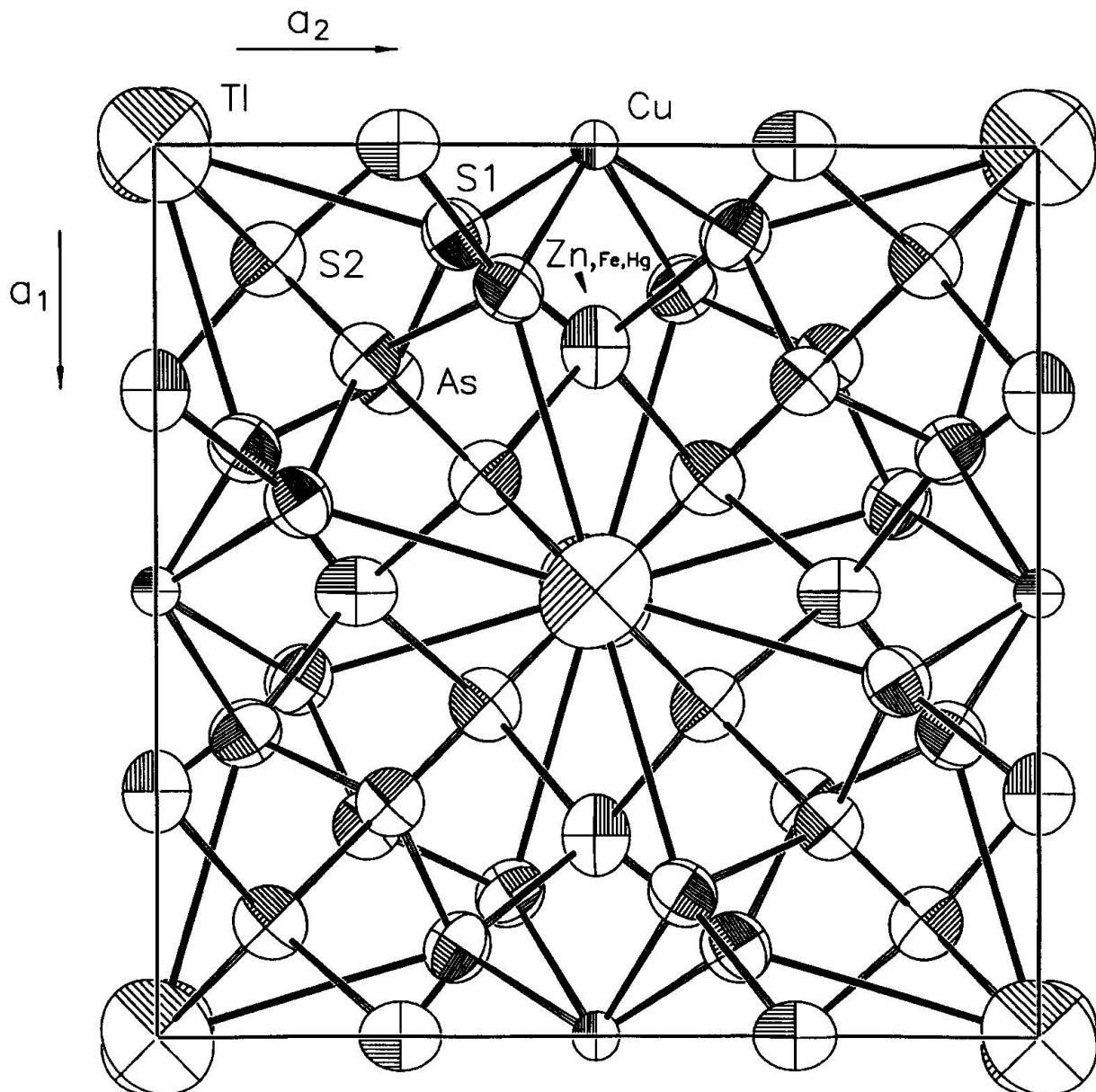


Fig. 3 Projection of the stalderite structure // c-axis.

7. Structure determination and refinement.

The analysis of the corrected intensity data for systematic absences and internal consistency of the equivalent reflections confirmed both the body centered lattice and within the Laue class 4/mmm the five possible spacegroups: I42m, I4m2, I422, I4mm, I4/mmm, as proposed from previous film methods.

The statistical distribution of the normalized $|E^2-1|$ -value (0.786) showed a good agreement with the theoretical value (0.736) for an acentric structure. As a first attempt in solving this structure, we used the most probable symmetry, I42m. Whereas direct methods failed, the structure was solved by a computerized three-dimensional super-sharp Patterson superposition method implemented within the structure solution package SHELXS-92 (SHELDRICK, 1992) which was available to us as a pre-version.

For the subsequent structure refinement we used the γ -version of SHELXL-92 which is based on F^2 . From 358 unique reflections, 296 were measured with $F^2 > 2\sigma(F^2)$. The "final" $R(F)$ -value of 0.047 and standard deviations which are comparable with conventional X-ray measurements may be somewhat surprising, since common arguments such as incorrect absorption or extinction correction are not valid in the case of this small crystal. We think, this is due to the "bad reflection profiles" mentioned above which could not be perfectly corrected. For this reason table 6 gives besides the fractional atomic coordinates only the isotropic temperature factors.

For the same reason in table 7 the inter-atomic distances are presented without the angles, since the latter are extremely sensitive on small shifts of the atomic coordinates. From the refinement of the structure and of the occupation factors of the (Zn,Fe,Hg) position the formula of stalderite is calculated to be: $TiCu(Zn_{1.16}Fe_{.46}Hg_{.38})As_2S_6$.

8. Description of the structure

A projection of the structure // c-axis is shown in figure 3. The $TiAs_2S_6$ -polyhedron is presented in figure 4.

The arrangement of the S atoms around the Ti shows a $(2 + 4)$ coordination which can be described as an orthorhombic pyramid with a split apex. Four S(1) atoms form a rectangular base with identical Ti-S(1) bond-lengths of 3.500 Å. Ti is slightly shifted from the center of the base towards the split apex, occupied by two S(2) atoms with Ti-S distances of 2.959 Å (mean Ti-S = 3.320 Å). This type of coordination polyhedron is not known from Ti-As-sulfosalts so far. As shows the well known trigonal pyramidal coordination with three S atoms, two S(1) and one S(2), forming the base and the As at the apex (mean As-S = 2.297 Å). These sulfur atoms are also part of the Ti polyhedron. One Ti polyhedron and two symmetry equivalent As polyhedra build a mixed metal-coordination polyhedron having the formula $TiAs_2S_6$ by sharing common faces (Fig. 4). The Ti-As distances of 3.484 Å in stalderite are

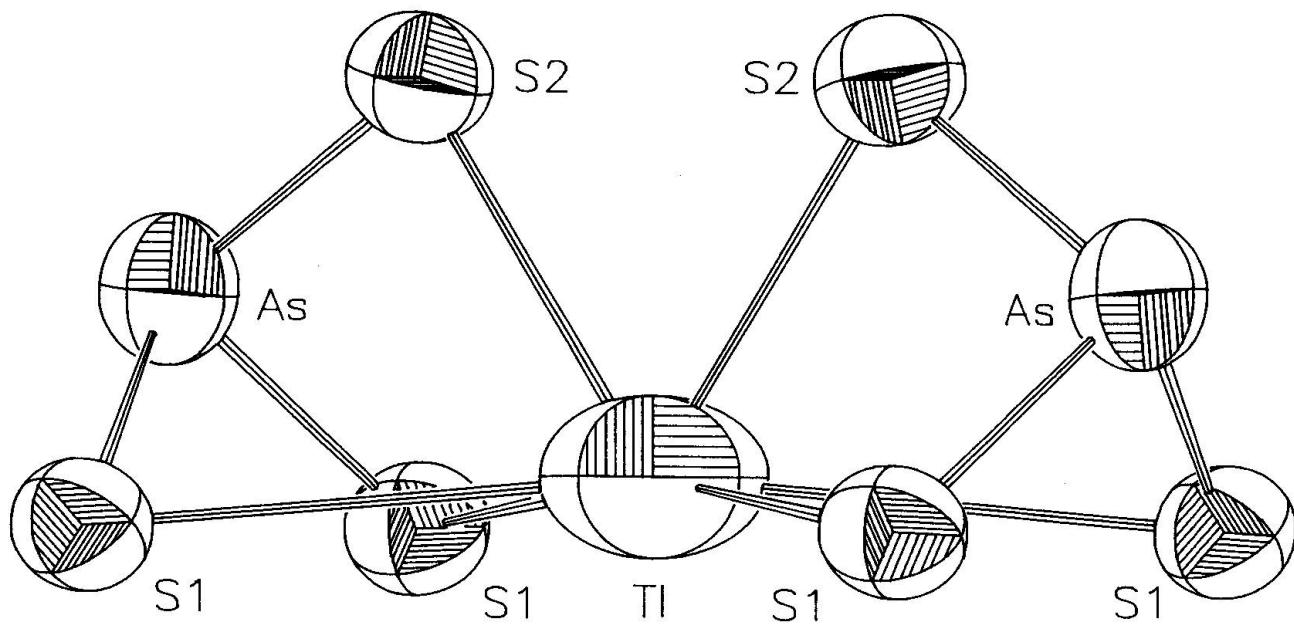


Fig. 4 The $TiAs_2S_6$ -polyhedron in stalderite.

within the range of 3.3 to 3.6 Å as found in other (Tl-As)-sulfosalts. Additionally the structure shows a remarkably short Tl-Tl distance of 3.279 Å suggesting Tl-Tl interactions as proposed by FLEET (1973). Both, the Cu- as well as the (Zn,Fe,Hg)-atoms are surrounded by four S atoms forming slightly distorted tetrahedra (mean Cu-S = 2.357 Å, mean [Zn,Fe,Hg] = 2.406 Å). The analysis of Cu-S distances in approximately 20 other Cu-bearing sulfosalts yields a mean value of 2.34 Å (EDENHARTER, 1976), which is in good agreement with the present investigation. An equivalent comparison cannot be done in the case of Zn-S distances due to the lack of sufficient crystal data available so far.

The basis of the stalderite structure is a three-dimensional network formed by the CuS_4 and the $(\text{Zn},\text{Fe},\text{Hg})\text{S}_4$ tetrahedra, sharing common corners. This network shows channels // c-axis in which the Tl and the As atoms, located at the positions (0,0,z) and (x,x,z) respectively, build mixed metal-polyhedra (TiAs_2S_6) as described above. These polyhedra stabilize the network by sharing corners and edges with the CuS_4 and the $(\text{Zn},\text{Fe},\text{Hg})\text{S}_4$ tetrahedra.

With S:As = $\varphi = 3$ the structure of stalderite with isolated trigonal BS_3 -pyramids belongs to group II a1 of the classification proposed by NOWACKI (1969). A subsequent determination of the crystal structure of routhierite (WULF et al., 1995) confirmed our assumption that the structures of routhierite and stalderite are isotypic. A detailed comparison of the two structures appears in a separate paper.

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