

Zeitschrift: Verhandlungen der Schweizerischen Naturforschenden Gesellschaft.
Wissenschaftlicher und administrativer Teil = Actes de la Société
Helvétique des Sciences Naturelles. Partie scientifique et administrative
= Atti della Società Elvetica di Scienze Naturali

Herausgeber: Schweizerische Naturforschende Gesellschaft

Band: 153 (1973)

Vereinsnachrichten: Sektion für Kristallographie

Autor: [s.n.]

Nutzungsbedingungen

Die ETH-Bibliothek ist die Anbieterin der digitalisierten Zeitschriften auf E-Periodica. Sie besitzt keine Urheberrechte an den Zeitschriften und ist nicht verantwortlich für deren Inhalte. Die Rechte liegen in der Regel bei den Herausgebern beziehungsweise den externen Rechteinhabern. Das Veröffentlichen von Bildern in Print- und Online-Publikationen sowie auf Social Media-Kanälen oder Webseiten ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. [Mehr erfahren](#)

Conditions d'utilisation

L'ETH Library est le fournisseur des revues numérisées. Elle ne détient aucun droit d'auteur sur les revues et n'est pas responsable de leur contenu. En règle générale, les droits sont détenus par les éditeurs ou les détenteurs de droits externes. La reproduction d'images dans des publications imprimées ou en ligne ainsi que sur des canaux de médias sociaux ou des sites web n'est autorisée qu'avec l'accord préalable des détenteurs des droits. [En savoir plus](#)

Terms of use

The ETH Library is the provider of the digitised journals. It does not own any copyrights to the journals and is not responsible for their content. The rights usually lie with the publishers or the external rights holders. Publishing images in print and online publications, as well as on social media channels or websites, is only permitted with the prior consent of the rights holders. [Find out more](#)

Download PDF: 05.08.2025

ETH-Bibliothek Zürich, E-Periodica, <https://www.e-periodica.ch>

10. Sektion für Kristallographie

Schweizerische Gesellschaft für Kristallographie
Société Suisse de Cristallographie
Società Svizzera di Cristallografia

Präsident: Dr. E. Ascher, Battelle, 7, route de Drize, 1227 Carouge
Sekretär: Dr. P. Engel, Sahlistrasse 6, 3000 Bern

Die Vortragenden sind mit * bezeichnet / Les conférenciers sont indiqués par *

Wissenschaftliche Sitzung / Séance scientifique

Samstag, 20. Oktober / Samedi 20 octobre

1. T. Ito, W. Nowacki* (Dept. of Crystal and Struct. Sciences, University of Bern): The crystal structure of freieslebenite, PbAgSbS_3

The crystal structure of freieslebenite, PbAgSbS_3 , has been determined with three-dimensional counter data ($R = 3.2\%$). The structure was solved by the method of key shifts. The obtained structure is different from the model proposed by Hellner (1957); instead, it is isomorphous with marrite, PbAgAsS_3 , an As-analogue of freieslebenite. The crystal is monoclinic, space group $\text{P}2_1\text{a}$, with $a = 7.518(1)$, $b = 12.809(4)$, $c = 5.940(1)$ Å, $\beta = 92.25(1)^\circ$ and $Z = 4$.

The structure is a superstructure of a PbS-type substructure. The displacements of the atoms from the ideal substructure are less in freieslebenite than in marrite, probably because of the larger atomic radius of Sb than that of As. Sb has the usual trigonal-pyramidal coordination of S atoms. The Sb–S distances are 2.431, 2.453 and 2.480 (4) Å. The SbS_3 pyramids are isolated from each other. Pb is coordinated with six S atoms in a distorted octahedral arrangement. The Pb-S distances range from 2.806 to 3.167 (4) Å. Ag has three nearest S neighbours at the distances, 2.522, 2.575 and 2.687 (4) Å. The AgS_3 group is nearly planar. A fourth S atom is at a distance of 2.928 (4) Å from Ag, the Ag–S being approximately perpendicular to the AgS_3 plane. The temperature factor of Ag is significantly larger and more anisotropic than those of the other atoms; this feature is common among related structures (Z. Krist. 139 (1974) 85-102).

2. Jan C. Portheine*, Werner Nowacki (Dept. of Crystal and Struct. Sciences, University of Bern): On the crystal structure of zinckenite

The crystal structure of the mineral sulfosalt zinckenite, $\text{Pb}_6\text{Sb}_{14}\text{S}_{27}$, has been refined to a final R value of 0.13 on the basis of 956 reflexions. The intensities were collected on a crystal from Cerro Bonete (Bolivia), with the aid of a Supper-Pace autodiffractometer, using Cu radiation.

The Bragg reflexions correspond to a hexagonal unit cell, with dimen-

sions: $a = 22.148(6)$ and $c = 4.333(6)$ Å, which contains $1\frac{1}{2}$ formula units. Additional diffuse intensity indicates the presence of a one-dimensional ordering in the structure with a period of $2c$.

Results of position refinements in the possible space groups $P6_3/m$ and $P6_3$ [$00l$ absent for l odd] have been compared according to Hamilton's significance test on R factors. The latter space group is the correct one, but there are indications for a local symmetry corresponding to $P6_3/m$ around the c axis.

One of the cation has the mixed occupancy of 0.38 Pb plus 0.50 Sb. The one-dimensional ordering may consist in alternating occupancy by Pb and Sb of the position of this ion in consecutive cells along c . This ion is coordinated by six S ions arranged in a trigonal prismatic way and two additional S ions outside the prism on normals to two side faces. Three of these S ions are symmetry equivalents of S(1) which has an occupancy of 0.75 and the coordination number of the central ion is therefore $7\frac{1}{4}$.

There are three independent Pb ions in the structure. Pb(1) has a similar coordination as the mixed cation and a coordination number of 8. The remaining ions, Pb(2) and Pb(3) have occupancies of 0.19 and 0.18 respectively and coordination numbers 9. Six of the coordinating ions form a trigonal prism and the other three lie on normals to the three side faces of this prism. The average cation-anion distances in the coordination polyhedra are 3.10 Å for the mixed cation and 3.14 Å for the Pb ions. The three independent Sb ions occur as tops of trigonal pyramids with S ions at the basis corners. Average Sb—S distances in the pyramids are 2.59, 2.55 and 2.51 Å for Sb(1), Sb(2) and Sb(3) respectively.

The coordination prisms of the Pb ions and the mixed cation have their axes parallel to c . Prisms of the same ion in adjacent cells along c are stacked in top of each other into infinite columns parallel to c . Three columns of Pb(1) prisms together form a threefold column about the threefold axis. In this case the elementary prisms share two of the three parallel edges and so a composition of PbS_4 for the multiple column is established. About the 6_3 axis six columns of the mixed cation form a six fold ring wall in such a way that single-column neighbours are shifted over $\frac{1}{2}c$ with respect to each other. The ions Pb(2) and Pb(3) are enclosed by this ring wall.

The Pb(1) multiple columns and the ring walls are joint by endless spirals of SbS_3 pyramids. The spirals of composition SbS_2 are winding about the 2_1 axes and consist of six pyramidal units per winding period, which is equal to c .

According to Nowacki's topological classification of sulfosalts the constellation of SbS_3 units in endless spirals is to be expected when the ratio φ of the numbers of S and Sb ions is equal to 2. That this constellation is found in zinckenite, which has $\varphi = 1.93$, may be due to the partially occupied ionic positions in the structure. Zinckenite belongs to type $V \cdot 1 \cdot a_2$ ($1 < \varphi < 2$) of the above mentioned classification [endless chains plus additional S's].

3. T. Srikrishnan*, W. Nowacki (Dept. of Crystal and Struct. Sciences, University of Berne): Refinement of the crystal structure of livingstonite, HgSb_4S_8

The crystal structure of livingstonite has been redetermined with a view to confirm the new chemical formula, HgSb_4S_8 (not HgSb_4S_7) and also to study the coordination of Hg and the S–S bond in the structure, reported by Niizeki and Buerger (1957). Crystals of livingstonite are monoclinic, having the cell dimensions $a = 30.567 \pm 0.006$, $b = 4.015 \pm 0.001$, $c = 21.465 \pm 0.003$ and $\beta = 103.4 \pm 0.0^\circ$. The space group is $C_{2h}^6 - A2/a$ and there are eight formula units in the structure. The structure was refined by block-diagonal least squares method to a final R value of 0.073 for the observed 596 reflections (0.102 for all 1099 reflections).

The structure confirms the new chemical formula. There is a S_2 group with a S–S distance of 2.06 Å, which gives raise to the additional sulfur atom in the new chemical formula. There are two kinds of layers running $\parallel c$ in the structure. The S–S bond cements two Sb_2S_4 double chains, so as to form a S_2 group between them. This S_2 group is located in the structure in such a way that its middle point is at a pseudo centre of symmetry. The other two Sb_2S_4 double chains are bridged together by the Hg atoms. The bonds between these two double chains are rather weak and hence explain the presence of a perfect cleavage $\parallel (001)$.

The coordination of the Hg atoms is a distorted octahedron, two of the S atoms of which are strongly and linearly bonded, similar to that observed in the structure of cinnabar, HgS . In Hg(1) these two linear bonds are at a distance of 2.52 Å, whereas in Hg(2) they are at a closer distance of 1.90 Å. The average Hg–S distances are 3.04 and 2.89 Å respectively for the two Hg atoms and the average standard deviations are 0.013 and 0.02 Å respectively.

There are four independent Sb atoms in the structure. Sb(1) has a coordination of 4 S which could be described as a distorted trigonal pyramid plus an additional S. These Sb–S distances are in the range 2.38 to 2.93 Å and have a mean standard deviation of 0.02 Å. Sb(2) has 5 S in the range 2.58 to 2.94 Å forming a square pyramidal configuration, with the Sb atom almost at the centre of the basal plane and one S at the apex. The average standard deviation in these Sb–S distances is 0.02 Å. Sb(3) has the familiar trigonal pyramidal coordination, with 3 S in the range 2.3 to 2.85 Å, with a mean standard deviation of 0.02 Å. Sb(4), similar to Sb(1), has 4 S in the range 2.4 to 2.98 Å, which could be described as a trigonal pyramid plus an additional S. The mean standard deviation in these distances is 0.02 Å.

The structure of livingstonite could be expressed as $[(\text{Sb}_2\text{S}_4)_2\text{Hg}^{\text{VI}+\text{VI}}]$ and belongs to the type IV. a_1 , in the classification of the sulfosalts by Nowacki (1969).

- 4.** D.J.E. Mullen, W. Nowacki* (Dept. of Crystal and Struct. Sciences, University of Bern): The crystal structure of aramayoite

The crystal structure of aramayoite of the ideal composition $\text{Ag}(\text{Sb}, \text{Bi})\text{S}_2$ was determined using non-integrated photographic data. The cell dimensions are: $a = 7.76 \pm 0.02 \text{ \AA}$, $b = 8.85 \pm 0.02 \text{ \AA}$, $c = 8.23 \pm 0.02 \text{ \AA}$, $\alpha = 100^\circ 11' \pm 15'$, $\beta = 90^\circ 43' \pm 15'$, $\gamma = 103^\circ 50' \pm 15'$. The space group is P1. The final R -factor was 11.9% for 418 observed reflections.

Aramayoite has a superstructure, and the substructure has a rock-salt type arrangement. The structure is statistical, with partial and complete substitution of antimony atomic sites by bismuth. The unit cell content is found to correspond with the formula unit $\text{Ag}_5\text{Sb}_{3.75}\text{Bi}_2\text{S}_{12}$ (valence rule not fulfilled). There are three types of layers in the unit cell, an antimony/bismuth layer, a silver layer, and a mixed layer consisting of all three types of metal atoms.

The mean bond distances are 2.55(8) Å for Ag–S, 2.66(8) Å for Sb–S and 2.77(7) Å for Bi–S.

Aramayoite has a certain similarity with matildite, AgBiS_2 . Both are layer structures with pronounced cleavages. But in the case of matildite, the layers are alternate Ag, Bi, S, with metal layers in between sulfur layers. Both have distorted rock-salt type substructures with statistical superstructures (Z. Krist. 139 (1974) 54–69).

- 5.** Ch. Bärlocher*: Bestimmung der Kristallstruktur des synthetischen Zeolithes F mittels Pulverdaten
- 6.** H. Möck*: Koordinationssequenzen und Radialverteilungsfunktion zur Charakterisierung von Zeolithgerüsten
- 7.** S. Veprek*: Wachstum von TiN-Kristallen und Gradienten der inneren Energie im nichtisothermen Stickstoff/Chlor-Plasma
- 8.** D. Brinkmann*, J.L. Staehli: Phasenübergang und Tetraeder-Verzerrung im Anorthit
- 9.** A.G.M. Janner*: Ce qu'on peut apprendre en étudiant les translations non-primitives (conférence invitée)
- 10.** B. Prelesnik*, F. Gabela, R. Herak, I. Krstanovic, Lj. Manojlovic-Muir, K.W. Muir, B. Ribar: The crystal structure of three cobalt complex compounds
- 11.** T. Ozawa*, H. Shimazaki: The crystal structure of a new Bi-T compound from Tsumo Mine Japan

12. Y. Nakayama, K. Matsumoto*, S. Ooi, H. Kuroya: The crystal and molecular structure of bis (L-ornithinato) palladium (II)

13. F. E. Scarbrough, W. Nowacki* (Dept. of Crystal and Struct. Sciences, University of Bern): The molecular and crystal structure of (a) diketo, acetate derivative of peristyrene and (b) of [2₆]metacyclophane

(a) The crystal structure formed by unusual molecules C₁₇H₁₈O₄, a diketo acetate derivative of peristyrene, itself a key molecule in the proposed synthesis of dodecahedrane, has been solved by X-ray diffraction methods using the symbolic addition procedure. The crystals are monoclinic with space group P2₁/c—C₅2₁h, having cell dimensions $a = 11.6449$, $b = 10.9957$, $c = 14.2992 \text{ \AA}$ and $\beta = 133.31^\circ$. There are four molecules per unit cell giving a calculated density of 1.427 g/cm⁻³. The refinement by block diagonal matrix least squares with anisotropic temperature factors for non-hydrogen atoms led to a final R value of 0.057 for the 1946 observed reflections. The molecule has a bowl shaped structure whose base is a planar, regular carbon pentagon. One of the side pentagons bearing one of the carbonyl oxygens is distorted significantly from planarity and causes a deformation of the molecule from complete regularity.

(b) The crystal structure formed by [2₆]metacyclophane, C₄₈H₄₈, molecules has been solved by X-ray diffraction direct methods using a multiple solutions procedure. The crystals are monoclinic with space group C2/c and cell dimensions $a = 34.608$, $b = 5.334$, $c = 26.992 \text{ \AA}$ and $\beta = 124.1^\circ$. There are four molecules per unit cell; therefore the space group requires that the molecules have a center of symmetry. Block diagonal matrix least squares refinement led to a final disagreement factor of 0.09 for the 2115 observed reflections. The molecule has an open configuration which allows 1/3 *n*-hexane molecule per [2₆]metacyclophane to co-crystallize in “clathratelike” fashion at the center of the large ring. The CH₂ groups of one linkage pair in the asymmetric unit vibrate anisotropically along the b axis much more than the other two chemically equivalent pairs. The molecules are in contact with normal van der Waals distances.

14. P. Engel* (Bern): Beziehungen zwischen Intensitäten und Phasen beim Beugungsbild eines begrenzten Musters

Durch die reellwertige Ortsfunktion $\varrho(x)$ werde ein eindimensionales, begrenztes Muster auf dem Intervall $(-\frac{1}{2}, \frac{1}{2})$ beschrieben. Das zugehörige Beugungsbild $\tilde{\mathfrak{F}}(s)$ ist die Fouriertransformierte von $\varrho(x)$

$$\tilde{\mathfrak{F}}(s) = \int_{-\frac{1}{2}}^{\frac{1}{2}} \varrho(x) e^{2\pi i s x} dx \quad (1)$$

und umgekehrt

$$\varrho(x) = \int_{-\infty}^{\infty} \mathfrak{F}(s) e^{-2\pi i s x} ds \quad (2)$$

Die komplexe Grösse $\mathfrak{F}(s)$ ist durch die Intensität $|\mathfrak{F}(s)|^2$ und die Phase $\alpha(s)$ bestimmt. Das Phasenproblem lässt sich so formulieren: Sind durch die Vorgabe der Intensitäten $|\mathfrak{F}(s)|^2$ auch bereits die Phasen $\alpha(s)$ festgelegt? Es werden nun einige grundlegende Beziehungen zwischen den Intensitäten und den Phasen aufgezeigt. Das Mischungsquadrat (Pattersonfunktion) ist

$$P(w) = P(-w) = \int_{-\infty}^{\infty} |\mathfrak{F}(s)|^2 e^{-2\pi i s w} ds = \int_{-\frac{1}{2}}^{\frac{1}{2}} \varrho(x) \varrho(x+w) dx \quad (3)$$

Zwischen den Momenten

$$M_{2n} = \int_{-1}^1 w^{2n} P(w) dw \quad (4)$$

und den Momenten

$$m_n = \int_{-\frac{1}{2}}^{\frac{1}{2}} x^n \varrho(x) dx \quad (5)$$

gilt dann die überaus einfache Beziehung

$$M_{2n} = \sum_{l=0}^{2n} (-1)^l \binom{2n}{l} m_{2n-l} m_l \quad (6)$$

Ist $\varrho(x)$ symmetrisch, $\varrho(x) = \varrho(-x)$, oder antisymmetrisch, $\varrho(x) = -\varrho(-x)$, so lassen sich aus Gl. (6) die Momente m_{2n} bzw. m_{2n+1} leicht berechnen. $\varrho(x)$ lässt sich in eine Reihe nach Legendreschen Polynomen entwickeln

$$\varrho(x) = A_0 \bar{P}_0(x) + A_1 \bar{P}_1(x) + A_2 \bar{P}_2(x) + \dots \quad (7)$$

wobei die Koeffizienten A_i durch die Momente m_k bestimmt sind. Eine gültige Lösung muss zudem die Besselsche Ungleichung

$$\sum_{n=0}^N \frac{A_n^2}{2n+1} \leq \int_{-\frac{1}{2}}^{\frac{1}{2}} \varrho^2(x) dx = P(0) \quad (8)$$

erfüllen.

Die Exponentialfunktion in Gl. (1) lässt sich durch eine Reihe nach MacLaurin darstellen

$$e^{2\pi i s x} = \sum_{n=0}^{\infty} \frac{(2\pi i s)^n}{n!} x^n \quad (9)$$

woraus unmittelbar die Beziehung folgt

$$\mathfrak{F}(s) = \sum_{n=0}^{\infty} \frac{m_n}{n!} (2\pi i s)^n \quad (10)$$

Zur Berechnung der Momente 4 wird die Potenz w^{2n} auf dem Intervall $(-1,1)$ in eine Fourierreihe entwickelt

$$w^{2n} = \frac{1}{2} K_{2n,0} + \sum_{h=1}^{\infty} K_{2n,h/2} \cos 2\pi h/2 w \quad (11)$$

Es gilt dann

$$M_{2n} = \frac{1}{2} K_{2n,0} |\mathfrak{F}(0)|^2 + \sum_{h=1}^{\infty} K_{2n,h/2} |\mathfrak{F}(h/2)|^2 \quad (12)$$

Für $h > 0$ lassen sich die Fourierkoeffizienten $K_{2n,h/2}$ durch die rekursive Formel

$$K_{2n,h/2} = \frac{4n}{(\pi h)^2} \left\{ (-1)^h - \frac{1}{2} (2n-1) K_{2n-2,h/2} \right\} \quad (13)$$

berechnen, wobei $K_{0,h/2} = 0$ ist. Für $h = 0$ ergibt sich unmittelbar

$$K_{2n,0} = \frac{2}{2n+1} \quad (14)$$

15. H. Grimmer*: Koinzidenzgitter und DSC-Gitter für kubische Kristalle

16. H. Flack*: Glissement dans des cristaux de polytetrafluoroéthylène

17. H. Flack, E. Parthé: Etude structurale des complexes thiocyanato et isothiocyanato de Ir(III)

18. J.-M. Moreau, E. Parthé: Etude structurale d'alliages Terre-Rate-Palladium ($T = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}$) pour des stoechiométries voisines de $T_5\text{Pd}_2$

19. M. Sauvage, E. Parthé: Prédiction de l'intensité diffusée dans les structures ternaires avec l'ordre à courte distance

20. K. Yvon*: L'application des méthodes directes aux structures hypersymétriques: la structure cristalline de $\text{Mo}_6\text{Ga}_{31}$

- 21.** A. Dunand*, R. Gerdil: Structure cristalline et moléculaire d'un complexe de l'or (III) sulphito coordonné
- 22.** G. Bernardinelli*, R. Gerdil: Structure cristalline et moléculaire d'un sucre pyrannosique insaturé ramifié
- 23.** H. Manohar, D. Schwarzenbach: Crystallographic studies of some diamino-piperidine complexes of divalent palladium
- 24.** R. Smith*, U. Aebi: Study of the structure of helical bio-crystals from electron micrographs
- 25.** U. Aebi*, R. Smith: Das Noise-Problem bei der Informationsextraktion aus elektronenmikroskopischen Bildern