

Plášil *et al.* Theuerdankite, a new silver mineral

Theuerdankite, Ag_3AsO_4 , a new mineral from the Alter Theuerdank Mine (St. Andreasberg), Germany

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Abstract

The new mineral theuerdankite, ideally Ag_3AsO_4 , was found in the Alter Theuerdank Mine, Beerberg, St. Andreasberg, Goslar District, Lower Saxony, Germany. Theuerdankite occurs as aggregates of anhedral grains up to 3 mm in size, growing in cavities of strongly supergene-weathered material consisting of native silver and chlorargyrite (but with calcite present). It is dark violet, changing to reddish and black when exposed to the air and light. It has a grey to violet grey streak; when readily fresh, its streak is brownish-red. The Mohs hardness is about 2. It is brittle without any observable cleavage or parting and with a conchoidal fracture. The calculated density is $6.622 \text{ g}\cdot\text{cm}^{-3}$. In reflected light, theuerdankite is dark grey with a pinkish tint, without any observable bireflectance, pleochroism, or anisotropy. It shows dark red internal reflections. The reflectance values for wavelengths recommended by the Commission on Ore Mineralogy of the IMA are (R %): 13.3 (470 nm), 12.8 (546 nm), 12.7 (589 nm), 12.5 (650 nm). The empirical formula (based on 4 *apfu*) is $\text{Ag}_{3.00}\text{As}_{1.00}\text{O}_4$. Theuerdankite is cubic, space group $P\bar{4}3n$, $a = 6.144(2) \text{ \AA}$, $V = 231.93(13) \text{ \AA}^3$ and $Z = 2$. The six strongest X-ray powder diffraction lines are [d_{obs} in Å , (I), hkl]: 3.0736, (22), 200; 2.7502, (100), 210; 2.5106, (55), 211; 1.7050, (36), 320; 1.6249, (44), 321; 1.3412,



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(17), 421. The crystal structure of theuerdankite ($R_1 = 1.69\%$ for 519 reflections having $I > 3\sigma(I)$), is isotopic to those of synthetic Ag_3AsO_4 and Ag_3PO_4 . The Gram-Charlier development describing the higher-order tensors representing the atomic displacement parameters of the silver atom was implemented, documenting that silver tends to behave in the theuerdankite structure anharmonically at room temperature.

Keywords: theuerdankite, new mineral, silver minerals, crystal structure, Gram-Charlier development, goodness-of-fit, St. Andreasberg

Introduction

Theuerdankite, ideally Ag_3AsO_4 , is a new silver mineral from the famous historic mining region of St. Andreasberg in Lower Saxony, Germany. It is named after the type locality, the Alter Theuerdank Mine. The new mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2023-009). The holotype specimen (polished section) of theuerdankite is deposited in the collections of the Department of Mineralogy and Petrology, National Museum in Prague, Cirkusová 1740, 193 00 Prague 9, Czech Republic under the catalog number PIP 59/2022. Here, we report on its description, including crystal structure refinement using a Gram-Charlier development describing the thermal movement of the silver atom in the crystal structure, which vibrates anharmonically around its equilibrium position. We also append a discussion on the proper handling of the diffraction data and the refinement.

Occurrence

Theuerdankite was found on a single specimen originating from the Alter Theuerdank Mine, Beerberg, St Andreasberg, Braunlage, Goslar District, Lower Saxony, Germany ($51^\circ 42' 29''$ N, $10^\circ 31' 41''$ E). This mine is among the important mines in the St. Andreasberg mining district and it is famous for the rich findings of the so-called “*buttermilch-erz*” = ore consisting of chlorargyrite. We refer to the paper by Schnorrer *et al.* (2009) for details on the occurrence and geology. Associated minerals within the studied specimen are chlorargyrite, native silver and calcite. Theuerdankite is most probably of supergene origin but could also be late hydrothermal if these fluids were oxidizing enough to convert As in the primary minerals to arsenates.

Physical and optical properties

Theuerdankite occurs as irregular aggregates up to 3 mm in size (Fig. 1), growing in cavities of strongly supergene-weathered material consisting of native silver and chlorargyrite. Its color is dark violet, changing to reddish and black when exposed to the air. It darkens when exposed to light. It has a grey to violet grey streak; when fresh, its streak is brownish-red. It is non-fluorescent in SW and LW ultraviolet light. The Mohs hardness is estimated at about 2 based on scratch tests. Theuerdankite is brittle; no cleavage and no parting were observed. The fracture is conchoidal. A density of $6.620 \text{ g}\cdot\text{cm}^{-3}$ for the empirical formula (WDS). Theuerdankite is dark grey with pinkish tints in reflected light with no visible birefractance and no pleochroism; no anisotropy has been observed. There are dark red internal reflections,

visible around fractures and inclusions of native silver (Fig. 2). Reflectance values measured in air using a spectrophotometer MSP400 Tidas at Leica microscope, with a 20× objective, are given in Table 1 and shown in Figure 3.

Chemical composition

Quantitative chemical analyses were carried out using a Cameca SX100 electron microprobe (WDS mode, 15 kV, 5 nA, 10 μm beam diameter) at the National Museum Prague, Czech Republic. The following standards and X-ray lines were used to minimize line overlaps: Ag (AgL_{α}), chalcopyrite (CuK_{α}), clinoclase (AsL_{α}) and fluorapatite (PK_{α}). Peak counting times were 20 s for all elements and 10 s for each background. The results obtained (average of 16 spot analyses) are given in Table 2. Contents of other elements with atomic numbers higher than that of C ($Z = 6$) are below detection limits. Matrix correction by PAP software (Pouchou and Pichoir, 1985) was applied to the data. The calculated empirical formula of theuerdankite based on 4 *apfu* and 4 O atoms is $Ag_{3.00}As_{1.00}O_4$. The ideal formula for theuerdankite is Ag_3AsO_4 , which requires Ag_2O 75.15 and As_2O_5 24.85, a total of 100.00 wt.%. It is soluble in a 25% ammonia solution and decomposes when heated up in a melting point tube without the evolution of H_2O .

Raman spectroscopy

The Raman spectra of theuerdankite were collected in the range 50–4000 cm^{-1} using a DXR dispersive Raman Spectrometer (Thermo Scientific) mounted on a confocal Olympus microscope. The Raman signal was excited by an unpolarised green 532 nm solid state, diode-pumped laser and detected by a CCD detector. The experimental parameters were: 100× objective, 10 s exposure time, 100 exposures, 50 μm slit spectrograph aperture and 1 mW laser power level. The eventual thermal damage of the measured points was excluded by visual inspection of the excited surface after measurement, observation of possible decay of spectral features at the start of excitation, and checking for a thermal downshift of Raman lines. The instrument was set up using a software-controlled calibration procedure using multiple neon emission lines (wavelength calibration), multiple polystyrene Raman bands (laser frequency calibration), and standardized white-light sources (intensity calibration). Spectral manipulations were performed using the Omnic 9 software (Thermo Scientific).

The Raman spectrum of theuerdankite is given in Figure 4. The main bands observed are (in wavenumbers): 816, 787, 408, 337, and 82 cm^{-1} . The most prominent very strong Raman band at 787 cm^{-1} with a shoulder at 816 cm^{-1} is attributed to overlapping ν_1 (AsO_4)³⁻ symmetric stretching and ν_3 (AsO_4)³⁻ antisymmetric stretching vibrations. Raman band at 408 cm^{-1} is attributed to the ν_4 (AsO_4)³⁻ bending vibration. Raman band at 337 cm^{-1} is related to the ν_2 (AsO_4)³⁻ bending vibrations and those below 200 cm^{-1} to lattice modes (Vansant *et al.*, 1973; Nakamoto, 2009; Frost *et al.*, 2010; Čejka *et al.*, 2011). The observed bands are comparable to those in the infrared absorption spectrum of the synthetic Ag_3AsO_4 - 825, 785, 405 and 330 cm^{-1} (Hájek *et al.*, 1979; Muck *et al.*, 1980).

X-ray crystallography and structure refinement

X-ray powder diffraction data of theuerdankite were obtained using a pseudo-Gandolfi scan on XtaLAB Synergy R, DW system equipped with the HyPix-Arc150 detector, using monochromatic MoK α radiation from the microfocus rotating anode. The positions and intensities of diffractions were found and refined using the Pearson VII profile-shape function of the ZDS program package (Ondruš, 1993). The unit-cell parameters were refined by the least-squares program of Burnham (1962). The X-ray powder diffraction data of theuerdankite are given in Table 3. The refined unit-cell parameter (for the space group $P-43n$) is $a = 6.1448(3)$ Å, with $V = 231.01(2)$ Å³ and $Z = 2$.

Single-crystal X-ray diffraction data for theuerdankite were collected on XtaLAB Synergy, DW system equipped with the HyPix-Arc150 detector, using monochromatic MoK α radiation from the microfocus rotating anode from the same crystal as powder XRD data were collected. A fragment of the single crystal with approximate dimensions $85 \times 48 \times 28$ μm^3 was mounted on a glass fiber and analyzed. The complete data set (100% to the resolution of 0.4 Å) of the high-redundancy (>6) was collected using ω -scans (frame width of 0.5° and a counting time of 4 seconds per frame). Data reduction was performed using CrysAlisPro Version 1.171.43.111 (Rigaku, 2024). The data were corrected for Lorentz factor and absorption (multi-scan, ABSPACK scaling algorithm; Rigaku, 2024).

The structure of theuerdankite was solved from the intensity data using the intrinsic phasing by SHELXT program (Sheldrick, 2015) and refined using the software Jana2020 (Petříček *et al.*, 2023). The structure was refined as an inversion twin, and extinction (isotropic; Becker and Coppens, 1974) was also refined during the final stages of the refinement (Table 4). We used a Wilson modification to the least-square routine (weights) to avoid the statistical bias (Wilson, 1976). We employed the third-order anharmonic Gram–Charlier development (see for instance Volkov *et al.*, 2023) to describe the Debye–Waller factors for the Ag atoms, which improved the refinement considerably (see the Discussion). Refinement details are given in Table 4, atomic parameters (including atomic displacement parameters (ADP) and bond-valence sums calculated using parameters reported by Gagné and Hawthorne, 2015) are given in Table 5; the coefficients of the third-order Gram–Charlier development are given in crystallographic information file (cif); selected interatomic distances are reported in Table 6. The Vesta program (Momma and Izumi, 2011) was used to plot the electron density and the isosurface for ADPs of silver atoms.

The structure of theuerdenkite contains AsO₄ tetrahedra (Table 5) whose centers lie on lattice points of a *b.c.c.* lattice. The Ag1 atom occupies the 6*c* Wyckoff position, surrounded by four O atoms at a distance of 2.372(2) Å. The displacement of the Ag atom is slightly anisotropic with the general direction of vibration perpendicular to a plane formed approximately by four symmetrically related O1 atoms and assumes a pear-like shape (Fig. 6).

Related minerals and structures

The structure of theuerdankite is isotypic to that of synthetic Ag₃PO₄ (Ng *et al.*, 1978) and synthetic Ag₃AsO₄ (Weil, 2003). The electronic structure of the synthetic analog of theuerdankite has been investigated (e.g. Reunchan *et al.*, 2016; Li and Chen, 2017) due to its promising photocatalytic properties.

As a chemically related mineral, tetragonal tillmannsite, $(\text{Ag}_3\text{Hg})(\text{V},\text{As})\text{O}_4$ (Sarp *et al.*, 2003) could be considered. However, theuerdankite is structurally wholly distinctive. Tillmannsite contains isolated $(\text{V},\text{As})\text{O}_4$ tetrahedra and (Ag_3Hg) tetrahedral clusters. Clusters are specific for the disordered distribution of Ag and Hg atoms, which is a distinctive feature over chemically related synthetic compounds AgHg_2PO_4 and $\text{AgHg}_2\text{AsO}_4$ (Masse *et al.*, 1978) where Ag and Hg atoms are completely ordered and form the dimers $\text{O}_2\text{Ag}-\text{AgO}_2$ and $\text{O}_3\text{Hg}-\text{HgO}_3$. In tillmannsite, each (Ag,Hg) metallic atom is coordinated by three metallic neighbours and by three oxygens.

Also, cubic rudabanyaite, $(\text{Ag}_2\text{Hg}_2)(\text{AsO}_4)\text{Cl}$ (Effenberger *et al.*, 2019) can be viewed as a related mineral species but is structurally completely different. Its crystal structure is a framework based on by two crystallographically different $[\text{M}_4]^{4+}$ cluster cations forming tetrahedra ($M = (\text{Ag},\text{Hg})$ with a ratio $\text{Ag}:\text{Hg} \sim 1:1$), with no evidence for ordering between the Ag and Hg atoms. Small amounts of the M atoms are displaced by ~ 0.5 Å. Topologically, the barycentres of the $[\text{M}_4]^{4+}$ clusters and the As atom positions of the crystal structure of rudabányaite form a cubic primitive lattice with $a' = 1/2a = 8.68$ Å; half of the voids are occupied by Cl atoms.

Discussion

Harmonic vs. anharmonic refinement and adequate data handling

Initially, the structure of theuerdankite was refined using a harmonic approach to the displacement parameters of all atoms, thus described by the thermal ellipsoids. The final refinement converged smoothly (including isotropic extinction and inversion twin) to somewhat acceptable R -factors (comparison of harmonic and anharmonic refinement given in Table 4). However, one may suggest that the goodness-of-fit (GoF) from the harmonic refinement (GoF = 2.83 for all reflections) is rather high for a correct model and a reliable refinement. Nevertheless, these issues warrant further discussion. The standard approach to the goodness-of-fit and, consequently, a weighting scheme for the refinement is somewhat misleadingly applied by many users. The most widely used program for the structure refinement from the single-crystal X-ray data, SHELXL (Sheldrick, 2008), forces (if not changed by the user) the refinement to achieve a GoF value close to unity, namely by changing (refining) the weights. In contrast to this approach, the program Jana2020 (Petříček *et al.*, 2023) does not refine the weighting scheme but bases it purely on the experimental expectations (see *_refine_ls_weighting_details* in the CIF) that does not force GoF to be one. Therefore, in general, the GoF values obtained by Jana are usually larger than most of those reported by the SHELX program. The GoF values in Jana, however, do have a physical meaning. For example, if the final reported GoF is >2.0 , it does not automatically mean that the model is incorrect or entirely wrong. It just means that there are some features within a given dataset that the current model 1) does not describe/fit data well enough, or 2) there are systematic errors inherent to the diffraction data (from the measurement, for instance). Such undescribed features can include disorder (both positional or occupational), hidden twinning, modulation, or deformation of electron density (charge-density studies). Therefore, this approach also requires a careful and meaningful handling and evaluation of the diffraction data. In Jana, there are several ways of data handling, including different schemes and

approaches to averaging the reflection file for refinement (for details, see Petříček *et al.* 2014, 2023). Here, we used the refinement file obtained by averaging measured reflections using Poisson statistics. We used a refined instability factor value (= 0.010409), close to the most typical value of instability factor tested over the years of the Jana program development, which is 0.01 for the “non problematic” datasets. The actual value of the instability factor for the given diffraction dataset is deduced during the merging of reflections. The instability factor corrects the sigma values of individual/merged reflections obtained from the experimental reflection file provided by the diffractometer/data reduction program, such as they are fitted to the values obtained from merging statistics (Poisson). We recommend using the refined value of the instability factor for highly redundant datasets with expected reliable merging statistics. For comparison, we present here difference-Fourier maps obtained from the harmonic refinements with different weights (Figure 5a-c). It is apparent how the choice of the “proper” weights affects the results of the refinement (and in the worst case, the wrong choice of the weights can lead to biased refinement and interpretation). Finally, we relied on a refined value of the instability factor (corresponding map displayed in Figure 5b) and used it for the final refinement of the structure with an anharmonic approach to the atomic displacement parameters of silver (using a Gram-Charlier development). The final refinement converged to $R_1 = 1.69\%$ for 519 observed reflections and GoF of 1.54. The final difference-Fourier map is provided in Figure 6a; the highest residual density is located around the silver atom (Figure 6b). For comparison, the refinement with instability coefficient = 0.08 (overestimated!) would lead, in the case of anharmonic refinement, to $R_1 = 2.31\%$ for 519 observed reflections and a (alarming!) goodness-of-fit = 0.76 with corresponding difference-Fourier electron density of 0.56 and $-0.6 \text{ e}^-/\text{\AA}^3$.

Silver atoms seem to vibrate somewhat anharmonically (Figure 7) in the theuerdankite structure at room temperature, based on currently obtained high-resolution X-ray diffraction data. Investigating the silver behavior as a function of temperature would be thus very interesting. Nevertheless, this is beyond the scope of this paper and shall be subject to further studies.

The conditions of formation

The assemblage of native silver, chlorargyrite, calcite, and theuerdankite provides only limited clues about the conditions of the formation of the new mineral. Assuming that these minerals formed together, the presence of silver and chlorargyrite suggests that the redox conditions were near the Ag^0/Ag^+ redox boundary. The presence of calcite suggests that the solutions were near-neutral.

Since chlorargyrite is a fairly common secondary silver mineral, it can be asked if theuerdankite is indeed rare or if it is simply overlooked. In the absence of arsenates other than theuerdankite, no information about the activity of As(V) species in the aqueous solution can be extracted. The solubility of Ca arsenates (e.g., haidingerite) is too high and they are not a part of the observed mineral assemblage.

Thermodynamic properties of the synthetic Ag_3AsO_4 are known. Wagman et al. (1982) list $\Delta_f G^\circ = -542.6$ kJ/mol without references to the original source. Using the appropriate auxiliary data, the solubility constant $\log K_{\text{sp}}$ for Ag_3AsO_4 is



Wagman et al. (1982) also provided $\Delta_f G^\circ$ values for Ag_3PO_4 , Ag_2SO_4 , and AgCl . Inserting all these data into the thermodynamic database of the PHREEQC code (Parkhurst and Appelo 1999), some information can be extracted from available data on mine-drainage (MD) waters. Because Ag is rarely analyzed, only 20 analyses from almost 1200 analyses in our collection of MD waters yielded saturation indices for the Ag phases. Fig. 8a shows that the saturation indices (SI) for theuerdankite are consistently much lower than those of chlorargyrite. The difference is caused by the abundance of Cl^- as an anion in most waters. In fact, it is interesting that the SI values for chlorargyrite scatter around 0, meaning that this mineral controls Ag concentrations in the oxidized portions of ore bodies. From these limited data, it seems that theuerdankite can only form if the solutions initially contain Ag in excess of Cl (in molar proportions), such that the Cl concentrations are significantly depressed by the precipitation of AgCl . Hence, theuerdankite can be expected in secondary ores with abundant chlorargyrite and with some source of arsenate. Reduction of Ag^+ from the solution and precipitation of secondary native silver will not favor the formation of theuerdankite because it removes Ag, not Cl, from the solution.

Calculation of the saturation indices of the other phases (Fig. 8b) shows that the occurrence of Ag_3PO_4 is even less probable than that of Ag_3AsO_4 . The saturation indices are even lower, and such a potentially new mineral could only form in environments rich in chlorargyrite but unusually poor in arsenate. On the other hand, the saturation indices of Ag_2SO_4 are quite high but the availability of sulfate can be easily limited by precipitation of common secondary sulfates such as gypsum.

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Supplementary material. The supplementary material for this article can be found at

Competing interests. The authors declare none.

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Figure 1. Theuerdankite (1) from the type locality associated with native silver (2) and chlorargyrite (3) in the cavity of strongly supergene-weathered material; FOV 3.6 mm; photo M. Gross.

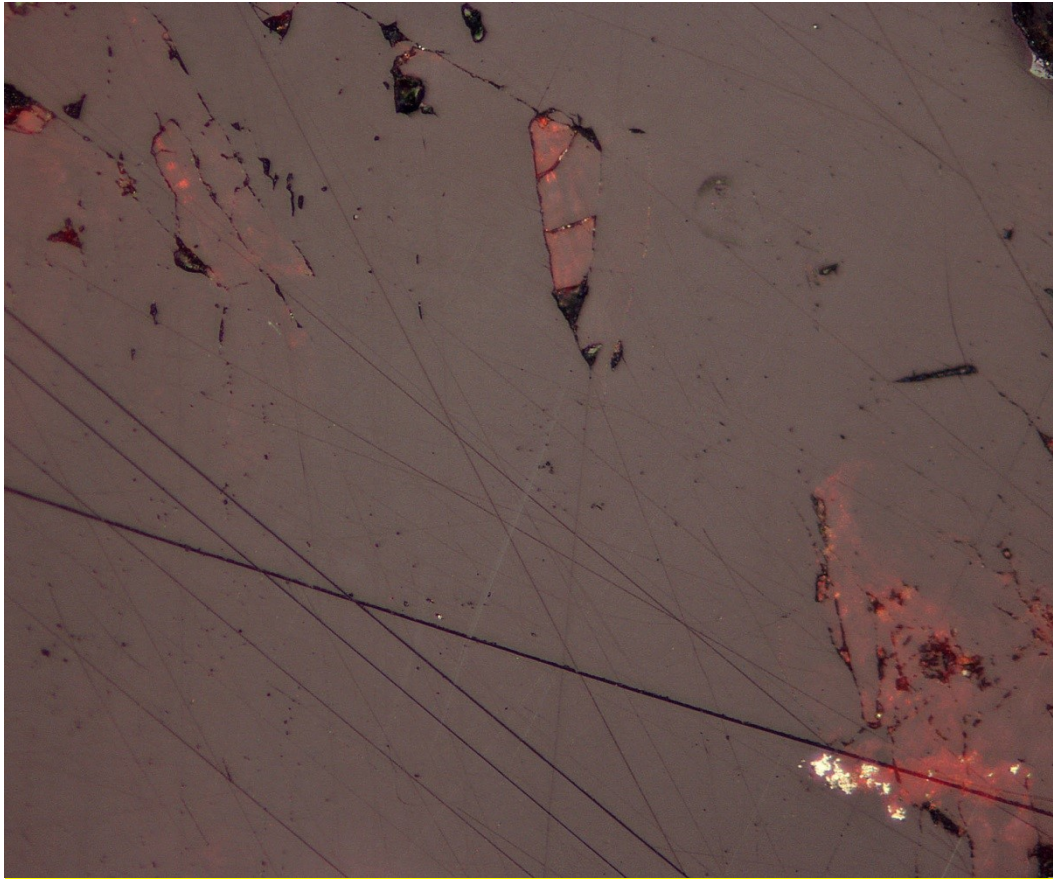


Figure 2. Dark-red internal reflections in theuerdankite visible especially around fractures and inclusions of native silver (white); field of view 700 μm ; photo in reflected light (partly crossed polars) by J. Sejkora.

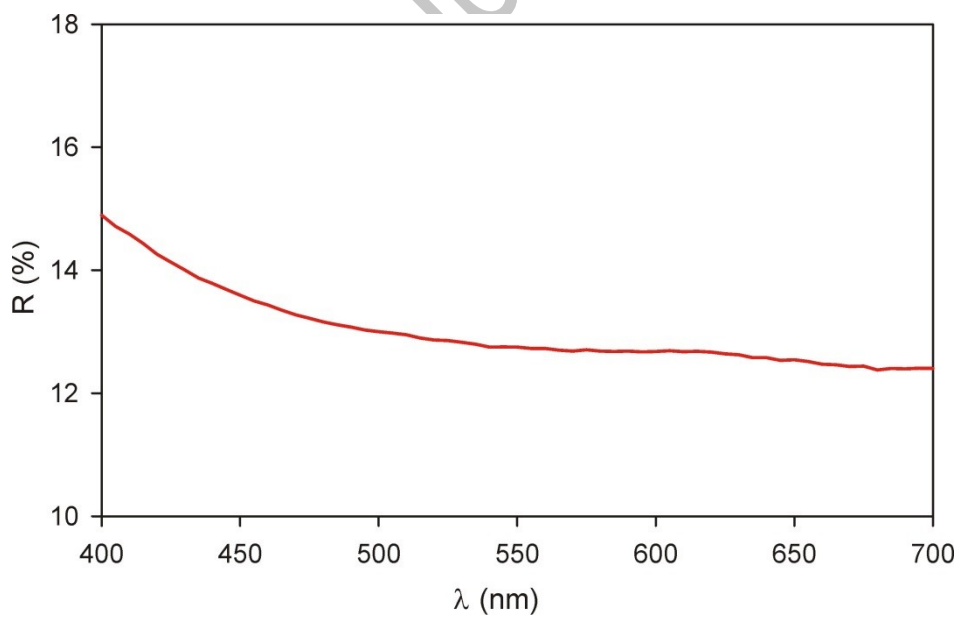


Figure 3. Reflectivity curve for theuerdankite from the Alter Theuerdank Mine, St Andreasberg.

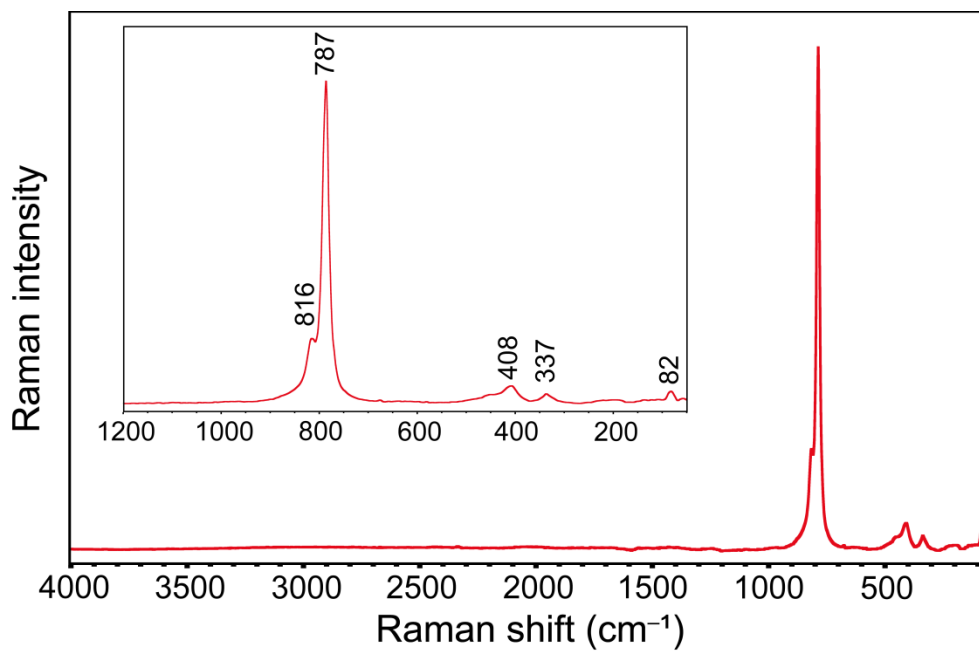


Figure 4. Raman spectrum of theuerdankite.

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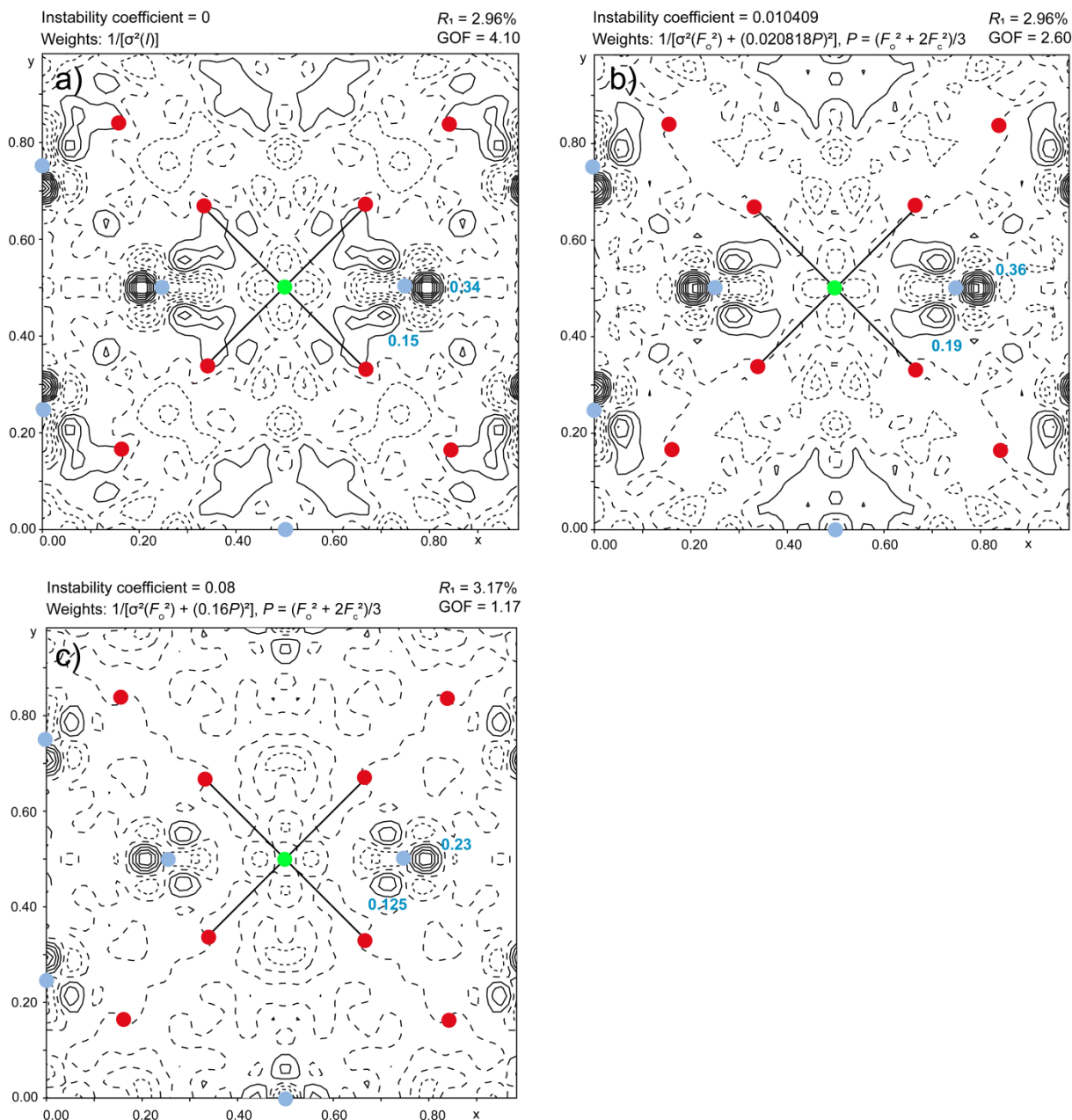


Figure 5. Difference-Fourier maps from the crystal structure refinements of theuerdankite using distinct weights (given) and harmonic approach to the ADP of silver. Color scheme: Ag = pale blue, As = green, O = red; solid lines = positive contours, dashed lines = negative contours; numbers (pale blue) = highest electron density ($e^{-}/\text{\AA}^3$). **A)** Refinement relying on statistics only returned a rather “noisy” difference map with too many features. **B)** Refinement using a refined value of the instability factor provides a less noisy and more “useful” difference Fourier map. **C)** Refinement with overestimated weights returns unrealistically “nearly clean” Fourier map and, accordingly, a low value of GOF. The selected weights for the final refinement were those used in **b)**.

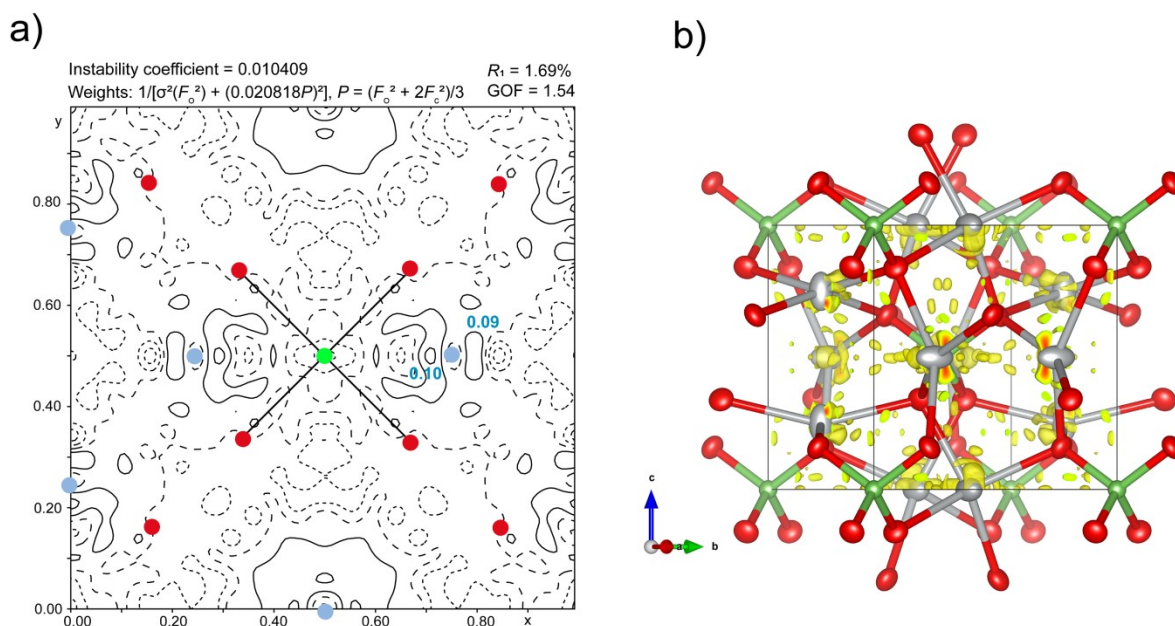


Figure 6. Difference-Fourier map from the final refinement of theurdankite structure using an anharmonic approach to the ADP of silver. The color scheme is the same as in the previous figure; the highest electron density is given in $e^-/\text{\AA}^3$. **A)** The Difference-Fourier map from the final refinement and **b)** its 3D representation was done in the Vesta program. Thermal ellipsoids given at the 75% probability level. Residual positive electron density is displayed in yellow color (isosurface).

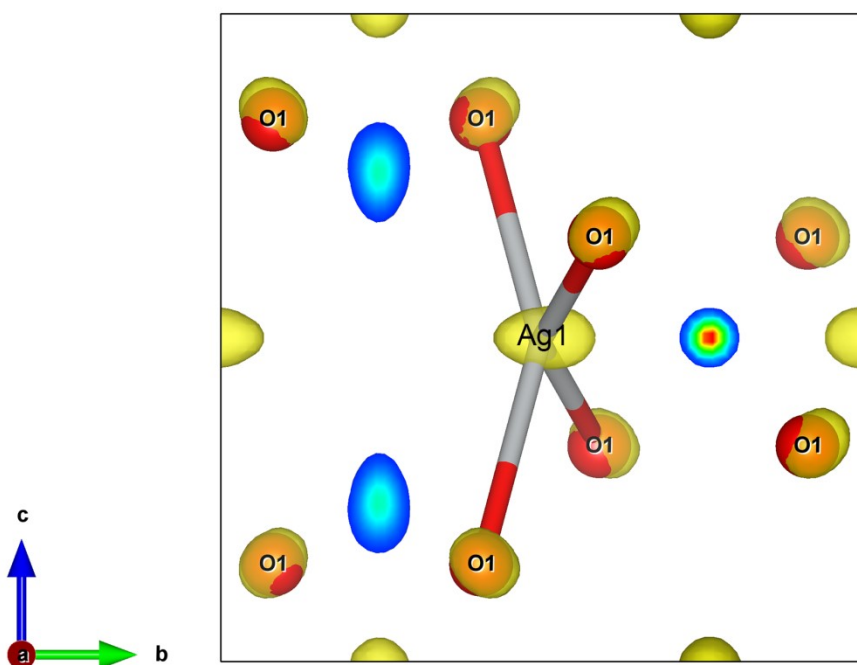


Figure 7. Representation of the anharmonic behavior of the ADP of silver at room temperature in the crystal structure of theurdankite as obtained from the non-harmonic refinement of the displacement parameters using *JPDF* maps.

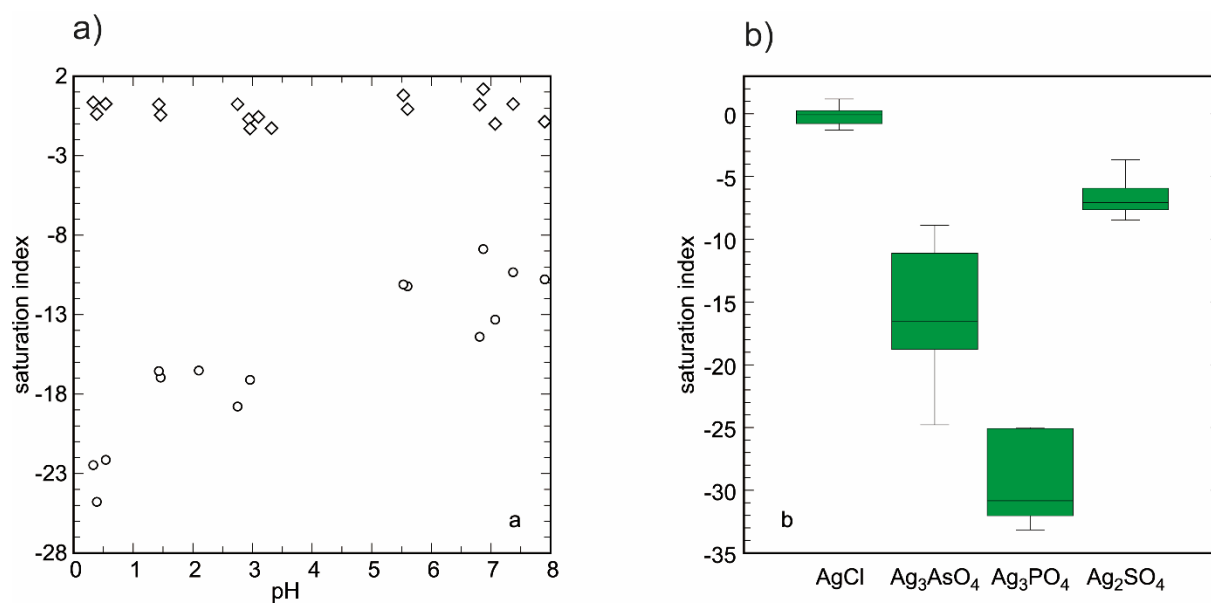


Figure 8. a) Saturation indices for chlorargyrite (diamonds) and theuerdankite (circles) in a range of pH values in mine-drainage waters. b) Box-and-whiskers diagrams that compare saturation indices of four Ag phases in mine-drainage waters. Boxes show the first and third quartile, the horizontal line the median, and the whiskers the total data range. Data in both a) and b) calculated with PHREEQC (Parkhurst and Appelo 1999), for details see text.

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Table 1. Reflectance data for theuerdankite*.

λ (nm)	<i>R</i> (%)	λ (nm)	<i>R</i> (%)
400	14.9	560	12.7
420	14.3	580	12.7
440	13.8	589	12.7
460	13.4	600	12.7
470	13.3	620	12.7
480	13.2	640	12.6
500	13.0	650	12.5
520	12.9	660	12.5
540	12.7	680	12.4
546	12.8	700	12.4

*The reference wavelengths required by the Commission on Ore Mineralogy (COM) are given in bold.

Table 2. Chemical composition (n = 12) (in wt.%) of theuerdankite.

Constituent	Mean	Range	S.D. (σ).
Ag ₂ O	75.22	74.64–6.19	0.46
CuO	0.03	0–0.25	0.08
As ₂ O ₅	24.80	24.22–25.45	0.35
P ₂ O ₅	0.04	0–0.23	0.08
Total	100.09		

S.D. - standard deviation

Table 3. X-ray powder diffraction data (d in Å) for theuerdankite; the six strongest diffractions are reported in bold.

$I_{obs.}$	$d_{obs.}$	$d_{calc.}$	$*I_{calc.}$	$*d_{calc.}$	h	k	l
1.9	4.3338	4.3450	0.5	4.3445	1	1	0
22.9	3.0736	3.0724	17.0	3.0720	2	0	0
100.0	2.7502	2.7480	100.0	2.7477	2	1	0
55.0	2.5106	2.5086	54.1	2.5083	2	1	1
3.2	1.9438	1.9431	3.4	1.9429	3	1	0
11.1	1.7744	1.7738	13.7	1.7736	2	2	2
35.7	1.7050	1.7043	25.8	1.7040	3	2	0
43.6	1.6429	1.6423	37.8	1.6421	3	2	1
12.1	1.5370	1.5362	13.3	1.5360	4	0	0
			0.8	1.4482	4	1	1
10.9	1.3746	1.3740	10.9	1.3738	4	2	0
16.9	1.3412	1.3409	23.8	1.3407	4	2	1
7.2	1.3103	1.3101	6.5	1.3099	3	3	2
13.5	1.1413	{ 1.1411	6.9	1.1409	5	2	0
		1.1411	13.7	1.1409	4	3	2
8.5	1.1217	1.1219	9.5	1.1217	5	2	1
8.0	1.0861	1.0863	10.9	1.0861	4	4	0
3.6	1.0240	{ 1.0241	1.3	1.0240	6	0	0
		1.0241	3.2	1.0240	4	4	2
1.2	1.0102	1.0102	4.5	1.0101	6	1	0
6.0	0.9967	{ 0.9968	6.5	0.9967	5	3	2
		0.9968	3.5	0.9967	6	1	1
0.3	0.9262	0.9264	4.1	0.9262	6	2	2
4.6	0.9159	{ 0.9160	6.3	0.9159	5	4	2
		0.9160	3.1	0.9159	6	3	0
1.9	0.9060	0.9060	3.4	0.9059	6	3	1
0.9	0.8872	0.8869	3.0	0.8868	4	4	4
2.1	0.8517	0.8521	1.3	0.8520	6	4	0
1.0	0.8440	{ 0.8441	2.3	0.8439	7	2	0
		0.8441	4.7	0.8439	6	4	1
		0.8362	3.0	0.8361	7	2	1
3.2	0.8361	{ 0.8362	1.6	0.8361	5	5	2
		0.8362	2.3	0.8361	6	3	3
1.9	0.7870	{ 0.7868	3.6	0.7867	6	4	3
		0.7868	1.8	0.7867	6	5	0
1.0	0.7802	{ 0.7804	2.6	0.7803	6	5	1
		0.7804	2.7	0.7803	7	3	2

$*I_{calc.}$; $*d_{calc.}$ - Intensity and d_{hkl} (in Å) calculated using the software *PowderCell2.3* (Kraus and Nolze, 1996) on the basis of the structural model given in Tables 4 and 5. Only reflections with $I_{calc} > 0.5$ are listed.

Table 4. Summary of data collection and refinements (harmonic/anharmonic) for theuerdankite.

	Harmonic	Cubic	Anharmonic
Crystal system		Cubic	
Space group		$P-43n$	
Unit-cell parameter a [Å]		6.132(2)	
Unit-cell volume [Å ³]		230.59(13)	
Z		2	
Calculated density [g/cm ³]	6.661 (for the formula from the structure)		
Crystal size [mm]		$0.085 \times 0.048 \times 0.028$	
Diffractometer	Rigaku XtalLab Synergy, DW system with HyPix Arc150 detector		
Temperature [K]		298	
Radiation, wavelength [Å]		MoK α , 0.71073	
θ range for data collection [°]		4.70–62.67	
Limiting Miller indices	$h = -15 \rightarrow 14, k = -14 \rightarrow 11, l = -15 \rightarrow 14$		
Axis, frame width (°), time per frame (s)		$\omega, 0.5, 5$	
Total reflections collected		4276	
Unique reflections		634	
Unique observed reflections, criterion		519, [$I > 3\sigma(I)$]	
Absorption coefficient [mm ⁻¹], type		19.63; multi-scan	
T_{\min}/T_{\max}		0.552/1	
Data completeness to θ_{\max} (%), redundancy, R_{int}		100, 6.744, 0.015	
Structure refinement	Full-matrix least-squares on F^2 by Jana2020		



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No. of param., restraints, constraints	9, 0, 0	11, 0, 0
R_1, wR_2 (obs)	0.0296, 0.0965	0.0169, 0.0568
R_1, wR_2 (all)	0.0384, 0.0978	0.0226, 0.0580
GOF obs/all	2.60, 2.83	1.54, 1.66
	$\sigma, w = 1/[(\sigma^2(F_o^2) + (0.020818P)^2], P = (F_o^2 +$	$\sigma, w = 1/[(\sigma^2(F_o^2) + (0.020818P)^2], P = (F_o^2 +$
Weighting scheme, weights	$2F_c^2)/3$	$2F_c^2)/3$
Extinction coefficient	370(60)	370(40)
Largest diffraction peak and hole ($e^-/\text{\AA}^3$)	2.89, -1.75	0.96, -1.08
Flack parameter; Friedel pairs	0.06(3)	0.038(17); 264

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Table 5. Atom positions, equivalent displacement parameters (in Å²) and bond-valence sums (BVS; in valence units) for theurdankite.

Atom	Wyckoff	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq}	BVS
Ag	6 <i>c</i>	1	0.25	0.5	0.02964(5)	1.059(2)
As	2 <i>a</i>	0.5	0.5	0.5	0.01133(3)	4.910(7)
O	8 <i>e</i>	0.65952(11)	0.34048(11)	0.34048(11)	0.01814(12)	2.022(4)

Table 6. Anisotropic displacement parameters (in Å²) for atoms in theurdankite structure.

Atom	<i>U</i> ¹¹	<i>U</i> ²²	<i>U</i> ³³	<i>U</i> ¹²	<i>U</i> ¹³	<i>U</i> ²³
Ag1	0.01916(6)	0.05058(11)	0.01916(6)	0	0	0
As1	0.01133(5)	0.01133(5)	0.01133(5)	0	0	0
O1	0.0181(2)	0.0181(2)	0.0181(2)	0.0033(2)	0.0033(2)	-0.0033(2)



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Table 7. Selected interatomic distances (in Å) in theuerdankite.

Ag–Ag	3.066(2) (2×)
Ag–Ag	3.7522(17) (8×)
Ag–O	2.3715(14) (4×)
Ag–O	3.4092(16) (4×)
As–O	1.6943(9) (4×)
O–O	2.7668(16) (3×)
O–O	3.444(2) (6×)

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