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Old defined minerals with complex, still unresolved structures: the case of stützite, $Ag_{5-x}Te_3$

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Abstract: The crystal structure of the mineral stützite, a relatively common silver telluride, was solved using intensity data collected using a crystal from the cotype material from the May Day mine, La Plata District, CO (USA). The study revealed that the structure is hexagonal, space group $P\overline{6}$, with cell parameters: $a = 13.454(2)$, $c = 8.459(1)$ Å and $V = 1326.0(5)$ Å^3. The refinement of an anisotropic model led to an R index of 0.0421 for 1950 independent reflections. In the crystal structure of stützite there are eight independent Te sites and eight Ag sites with $Z = 7$. Only Ag5, Ag6, Ag7 and Ag8 form classic metal-anion polyhedra: Ag8 is in linear coordination, Ag5 and Ag6 are triangularly coordinated, whereas Ag7 is in tetrahedral coordination. The case for Ag1, Ag2, Ag3 and Ag4 is more complicated as there are Ag–Ag contacts beside the typical bonds with the chalcogen. These positions correspond to low coordination (two, three and four) sites, in agreement with the silver preference for such environments. d^{10} silver ion distribution has been evidenced by means of a combination of a Gram-Charlier development of the atomic displacement factors and a split model. A discussion on the possible existence of different polytypes in stützite-like compounds and on the use of the non-harmonic approach based upon a Gram-Charlier development of the atomic displacement factors for the determination of disordered structures is also presented.

Keywords: crystal structure; disorder; polytypism; silver telluride; stützite.

Introduction

Stützite, $Ag_{5-x}Te_3$ ($x = 0.24–0.36$), is a relatively common mineral that forms in gold-silver vein, magmatic nickel and base metal sulfide deposits. It usually occurs with other tellurium-bearing minerals, particularly those in the system Ag–Te. For example, stützite coexists with hessite (Ag_2Te) and empressite (AgTe) (e.g. Huangshaping Pb-Zn deposit, P.R. China; [1]); hessite (e.g. Sulitjelma Cu-Zn deposit, Norway; [2]), native tellurium (e.g. Empress-Josephine Au-Ag deposit; [3]), and empressite (e.g. Empress-Josephine Au deposit; [4]). As a result of similar compositions and X-ray diffraction patterns between empressite and stützite and due to the inability of being able to so far synthesize empressite in the laboratory there has been some confusion concerning the physical and chemical differences between empressite and stützite. After about a century of debate on the real existence of empressite [3–12], its crystal structure has been determined [13] and it was definitely demonstrated that empressite and stützite have different crystal structures, notwithstanding the markedly different Ag to Te ratios of these tellurides.

The crystal structure of stützite was originally reported in the space group $P6/mmm$ [14], with hexagonal unit-cell parameters $a \sim 13.4$ and $c \sim 8.4$ Å. Subsequent studies on synthetic $Ag_{5-x}Te_3$ compounds by means of electron [15] and X-ray [16] diffraction pointed out the existence of a doubling of the **c**-axis and a disordered structural model in the acentric space group $P\overline{6}2m$. Such a model, however, included disorder also in the Te positions (partially-occupied sites) and only one Te atom (i.e. Te(10) in [16]) justified the doubling of the **c**-axis as the distribution of the other Te atoms was identical in both of the subcells ($c/2$). In addition, no electron diffraction patterns along [100] or [010] were reported by Kalin and Günter [15], thus casting doubts on the doubling of the **c**-axis in stützite. Also, the structural investigation of a stützite-like phase with formula $Ag_{12}Te_6S$ [17] showed that it crystallizes in the $P\overline{6}$ space group with hexagonal unit-cell parameters $a \sim 13.4$ and $c \sim 8.4$ Å, even though also these authors reported a completely disordered model involving both Ag and Te atoms.

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To help resolve the concerns relating to the structure of natural stützite, we present new crystal structure and chemical data for the mineral from a sample from the May Day mine, La Plata District, CO (USA). The sample is hosted in the mineral collection of the Harvard Mineralogical Museum (sample #108098), and labeled "redefined type material". Indeed, it was donated to the Museum by Honea [8] when he redefined both empressite and stützite.

Chemical composition

A preliminary chemical analysis using energy dispersive spectrometry, performed on the same crystal fragment used for the structural study (see below), did not indicate the presence of elements (Z > 9) other than Ag and Te. The chemical composition was then determined using wave-length dispersive analysis (WDS) by means of a Jeol JXA-8600 electron microprobe. Major and minor elements were determined at 20 kV accelerating voltage and 40 nA beam current, with 30 s as counting time. For the WDS analyses the following lines were used: Ag*L*α, Te*L*α. The estimated analytical precision is: ±0.20 for both Ag and Te. The standards employed were: Ag-pure element (Ag) and synthetic Sb_2Te_3 (Te). The stützite fragment was found to be homogeneous within analytical error. The average chemical composition (eight analyses on different spots) in wt% of elements is Ag 56.70 and Te 42.69 (Total 99.39). On the basis of three Te atoms, the formula of stützite can be written as $Ag_{4.71}Te_3$.

Tab. 1: Crystal data and summary of parameters describing data collection and refinement for the crystal structure of stützite.

Crystal data	
Formula	$Ag_{4.69}Te_3$
Crystal size (mm³)	0.045 × 0.055 × 0.070
Form	Block
Color	Black
Crystal system	Hexagonal
Space group	$P\bar{6}$ (#174)
a (Å)	13.454(2)
c (Å)	8.459(1)
V (Å³)	1326.0(5)
Z	7
Data collection	
Instrument	Oxford Diffraction Xcalibur 3
Radiation type	Mo*K*α (λ = 0.71073 Å)
Temperature (K)	293(3)
Detector to sample distance (cm)	6
Number of frames	1524
Measuring time (s)	50
Maximum covered 2θ (°)	65.38
Absorption correction	Multi-scan (*ABSPACK*; [18])
Collected reflections	2645
Unique reflections	1950
Reflections with $F_o > 4\sigma(F_o)$	965
R_{int}	0.0502
R_σ	0.0749
Range of *h*, *k*, *l*	$-19 \le h \le 14$, $-18 \le k \le 13$, $-12 \le l \le 11$
Refinement	
Refinement	Full-matrix least squares on *F*
Final R_1 [$I > 2\sigma(I)$]	0.0421
Final R_1 (all data)	0.0786
S	1.25
Number refined parameters	187
$\Delta\rho_{max}$ (e Å⁻³)	1.30
$\Delta\rho_{min}$ (e Å⁻³)	−1.64

X-ray crystallography and structure solution

Several crystals of stützite were selected from the sample #108098 and examined by means of a Bruker MACH3 single-crystal diffractometer using graphite-monochromatized Mo*K*α radiation and with an Oxford Diffraction Xcalibur 3 diffractometer, fitted with a Sapphire 2 CCD detector. The stützite crystals are very brittle and commonly intergrown with each other. In fact, most of them produced diffraction effects typical of multiple crystallites. A small crystal fragment (45 × 55 × 70 μm³) was selected for the single-crystal X-ray diffraction study. The intensity data collection (see Table 1 for details) was carried out by means of an Oxford Diffraction Xcalibur 3 single-crystal diffractometer (enhanced X-ray source, X-ray radiation Mo*K*α, λ = 0.71073 Å) fitted with a Sapphire 2 CCD detector. A total of 1524 frames of data were collected at room temperature as five sets of omega runs with an exposure time of 50 s per frame and a frame width of 1.00°. This afforded an overall data collection of 2645 reflections (1950 unique). The refined unit-cell parameters are *a* 13.454(2), *c* 8.459(1) Å and *V* 1326.0(5) Å³, which are similar to those originally reported by previous authors. Noteworthy, no doubling of the **c**-axis was observed, although we also collected overexposed precession images.

Data frames were processed using the *CrysAlis* software package [18] running on the Xcalibur 3 control PC. The program ABSPACK [18] was used for the absorption correction. The merging *R* for the data set in the Laue class 6/*m* decreased from 13.25% before the absorption correction to 5.02% after this correction. The statistical tests on the distribution of $|E|$ values strongly indicated the absence of an inversion center ($|E^2-1| = 0.745$), pointing to the choice of the space group $P\bar{6}$. We also did a first attempt to refine the structure, using JANA2006 [19], in the non-centrosymmetric $P\bar{6}2m$ space group using the atomic coordinates reported for synthetic stützite [16], modified according to a halving of the **c**-axis. The refinement of this model led an R index of about 0.21 and showed the presence of several partially-occupied Te sites. For this reason, we decided to begin a new structure solution in the space group $P\bar{6}$. We quickly found several ordered positions (mainly corresponding to the structure skeleton made by the Te atoms), but several Ag positions were highly disordered. Accordingly, split atoms were successively added at the positions found in the Fourier difference syntheses. However, with such a model and whatever the number of additional atoms it was not possible to obtain a residual value lower than *ca* $R = 0.13$, with residues ranging from –4.5 to 7.2 e$^-$/Å^3 around silver atoms and correlations being as high as 0.99. A different solution was then looked for in other crystal systems (trigonal and monoclinic), with concomitant twinning laws. Many trials involving various structure/space group combinations were tested, but they did not improve the F_{obs} versus F_{calc} agreement. Going back to the hexagonal system, $P\bar{6}$ space group, a non-harmonic approach with a Gram-Charlier development of the Debye-Waller factor [20, 21] was then attempted, with both the aim to reduce the number of refined positions and lower the correlation level and hopefully reach a convergence towards a reasonable structure model. A major improvement was achieved, on the one hand, by introducing fourth order tensors for three of the silver positions (i.e. Ag3, Ag5 and Ag6) and one tellurium position (i.e. Te8), which exhibited the most pronounced anisotropic displacement parameters (Figure 1). At this stage, with the introduction of racemic twinning, the residual R value smoothly converged to the $R = 0.0421$ value for 1950 reflections and 187 parameters, with residues <2 e$^-$/Å^3. Although the main structural topology of the refined model follow the symmetry of the space group $P\bar{6}2m$ (especially the Te positions), there are deviations which make the choice of $P\bar{6}$ preferable. It is worth noticing that the global amount of silver refined in the model (i.e. 4.69 Ag atoms per formula unit, considering $Z = 7$) is in excellent agreement with that found by electron microprobe analyses (i.e. 4.71). Atom coordinates and isotropic displacement parameters are given in Table 2. Anisotropic displacement parameters, non-harmonic displacement parameters and the list of observed and calculated structure factors for stützite are available as supplementary material.

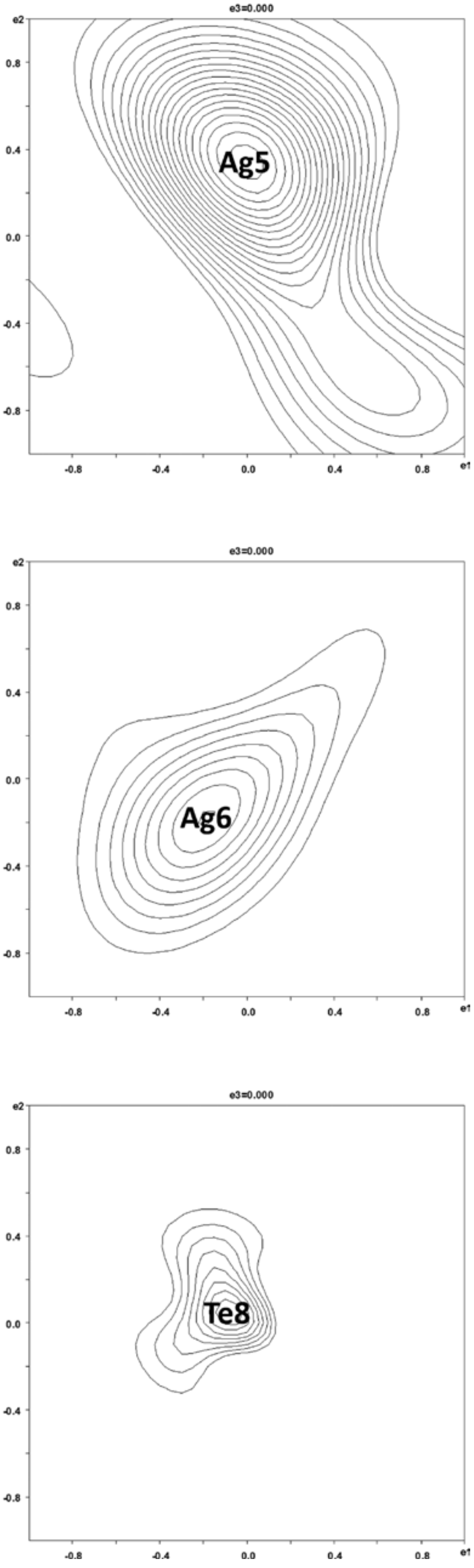

Fig. 1: Difference Fourier maps for stützite (classical anisotropic parameters), centered on Ag5, Ag6 and Te8. Contour lines in intervals of 0.5 e$^-$ × Å^{-3}.

Tab. 2: Atoms and Wyckoff positions, site occupancy factors (s.o.f.), fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for the selected stützite crystal.

Atom		s.o.f.	*x*	*y*	*z*	U_{eq}
Ag1	3*j*	1.00	0.2049(6)	0.5281(6)	0	0.036(3)
Ag2	3*j*	1.00	0.0108(7)	0.1368(7)	0	0.037(3)
Ag3	6*l*	1.00	0.226(2)	0.878(2)	0.241(3)	0.069(3)
Ag4	6*l*	0.81(2)	−0.1366(6)	0.5306(6)	0.2512(6)	0.039(3)
Ag5	6*l*	1.00	0.479(2)	0.918(3)	0.283(3)	0.078(5)
Ag6	6*l*	1.00	0.241(2)	0.142(3)	0.276(3)	0.056(5)
Ag7	3*k*	0.59(3)	0.2409(12)	0.7680(13)	½	0.045(7)
Ag8	3*k*	0.75(3)	0.0994(12)	0.9021(12)	½	0.060(7)
Te1	2*h*	1.00	1/3	2/3	0.2757(8)	0.030(2)
Te2	3*k*	1.00	0.3509(6)	0.0177(6)	½	0.033(3)
Te3	3*k*	1.00	0.0009(5)	0.6661(5)	½	0.028(3)
Te4	2*g*	1.00	0	0	0.2765(8)	0.028(2)
Te5	3*j*	1.00	−0.0343(5)	0.4550(5)	0	0.021(2)
Te6	3*j*	1.00	−0.1571(5)	0.2103(5)	0	0.020(2)
Te7	3*j*	1.00	0.2357(5)	0.3320(5)	0	0.031(2)
Te8	2*i*	1.00	2/3	1/3	0.2925(15)	0.068(3)

Tab. 3: Bond metal-chalcogen distances (Å) in the crystal structure of stützite.

Ag1-Ag3^{i}	2.92(3)	Ag4-Ag5^{i}	2.77(5)
Ag1-Ag3^{ii}	2.92(3)	Ag4-Ag6^{vi}	2.86(4)
Ag1-Te1	2.946(6)	Ag4-Te3	2.793(6)
Ag1-Te1^{iii}	2.946(6)	Ag4-Te8	2.674(6)
Ag1-Te5	2.857(10)		
Ag1-Te7	2.868(13)	Ag5-Te1	2.94(4)
		Ag5-Te3^{vi}	2.84(3)
Ag2-Ag6^{iv}	2.98(3)	Ag5-Te5^{vi}	2.83(3)
Ag2-Ag6^{v}	2.98(3)		
Ag2-Te4	2.934(8)	Ag6-Te3^{i}	2.94(3)
Ag2-Te4^{iii}	2.934(8)	Ag6-Te4	2.82(3)
Ag2-Te6	2.884(13)	Ag6-Te6^{vii}	2.84(3)
Ag2-Te7	2.846(8)		
		Ag7-Te1	2.949(16)
Ag3-Ag7	2.71(3)	Ag7-Te1^{viii}	2.949(16)
Ag3-Ag8	2.90(3)	Ag7-Te2	2.916(17)
Ag3-Te2	2.83(2)	Ag7-Te3	2.807(16)
Ag3-Te7^{vi}	2.62(2)		
		Ag8-Te2	2.934(15)
		Ag8-Te3	2.762(16)

(*i*) $-y+1, x-y+1, z$; (*ii*) $-y+1, x-y+1, -z$; (*iii*) $x, y, -z$; (*iv*) $-y, x-y, z$; (*v*) $-y, x-y, -z$; (*vi*) $-x+y, -x+1, z$; (*vii*) $-x+y, -x, z$; (*viii*) $x, y, -z+1$.

Results and discussion

Description of the structure

In the crystal structure of stützite there are eight independent Te sites and eight Ag sites with $Z=7$ (Figure 2). Only Ag5, Ag6, Ag7 and Ag8 form classic metal-anion polyhedra: Ag8 is in linear coordination, Ag5 and Ag6 are triangularly coordinated, whereas Ag7 is in tetrahedral coordination (Table 3). The case for Ag1, Ag2, Ag3 and Ag4 is more complicated as there are Ag–Ag contacts beside the typical bonds with the chalcogen.

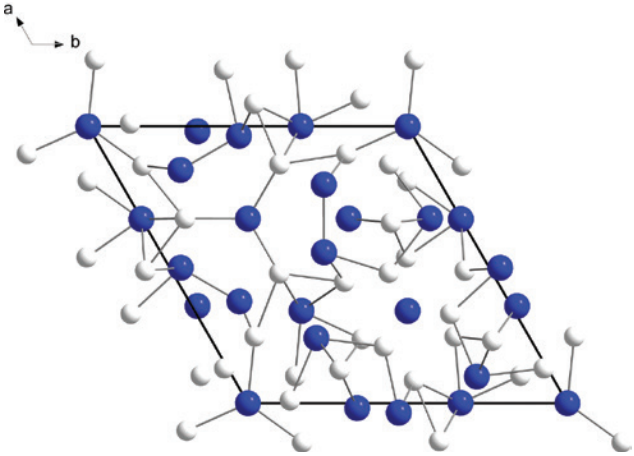

Fig. 2: General organization of the structure of stützite, as seen down **c**. White and blue spheres indicate Ag and Te, respectively.

As pointed out for the structure of synthetic $Ag_{12}Te_6S$ [17], the basic structural principles of stützite can also be evidenced by considering the type and number of distorted Frank-Kasper polyhedra formed by the Te atoms neglecting Ag atoms. Figure 3 shows the three types of Frank-Kasper polyhedra with coordination numbers 12 (icosahedron), 14 and 15, which constitute the Te partial structure by a systematic and space filling interpenetration. Each Te atom is at the same time central and peripheral atom of a polyhedron thus forming a topological close packing (Figure 4). Table 4 reports the coordination numbers and the distortions of the Frank-Kasper polyhedra estimated taking into account the range of interatomic distances between chalcogen atoms only. The shortest Te–Te contact of 2.85 Å is the typical dumbbell characterizing stützite. A similar feature (Te–Te < 2.9 Å) has been also observed in the structure of sylvanite ($AgAuTe_4$; [22]).

The large number of Frank-Kasper polyhedra generates several cavities for the Ag^+ ions. As it is well known, only a fraction of the cavities is actually occupied by Ag thus offering the ideal conditions for the observed dynamic disorder.

Possible existence of different polytypes?

The fact that several authors described stützite-like compounds as having a doubled **c**-axis raises the question

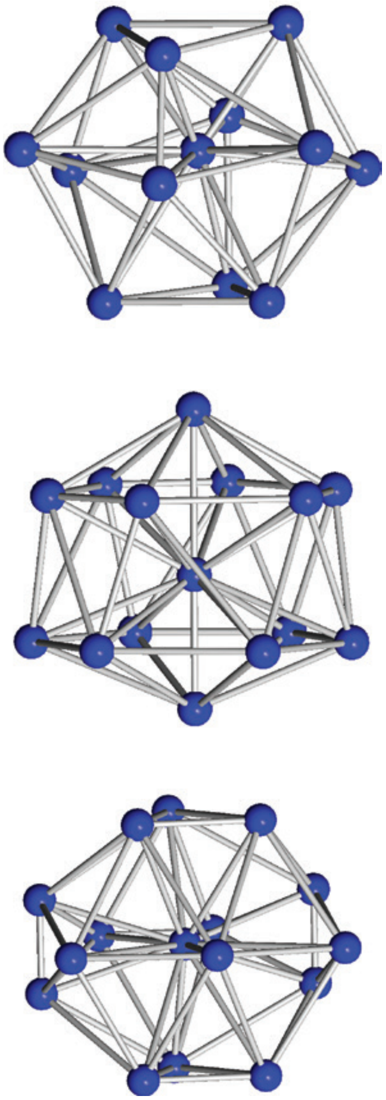

Fig. 3: Selected Frank-Kasper polyhedra in the structure of stützite formed by Te atoms. Top: coordination number 12 (Te5, Te6 and Te7); middle: coordination number 14 (Te1, Te4 and Te8); bottom: coordination number 15 (Te2 and Te3).

regarding whether different polytypes can exist. We think that when the non-stoichiometry of Ag in the $Ag_{5-x}Te_3$ formula is in the range $x = 0.24–0.36$ (as always reported for natural stützite), then the structure crystallizes in the space group $P\bar{6}$ with $c \sim 8.4$ Å, as determined in this study for the first time. When the non-stoichiometry is larger ($Ag < 4.64$), as in the sample studied by Peters et al. [16] with a composition $Ag_{4.53}Te_3$, then an ordering could occur (given the close similarity to the Ag_9Te_6 formula), leading to a doubling of the **c** axis. In this situation, the structure crystallizes in the space group $P\bar{6}2m$ with $c \sim 16.9$ Å. In this light, it would be interesting to check other stützite samples occurring in nature (with different provenances) to test if the Ag content is in fact responsible for a different polytype stabilization. Such a test should be quite straightforward as the X-ray powder pattern of a stützite showing the doubling of the **c** axis should exhibit well resolved superstructure diffraction peaks, as it was shown for synthetic $Ag_{12}Te_6S$ [17].

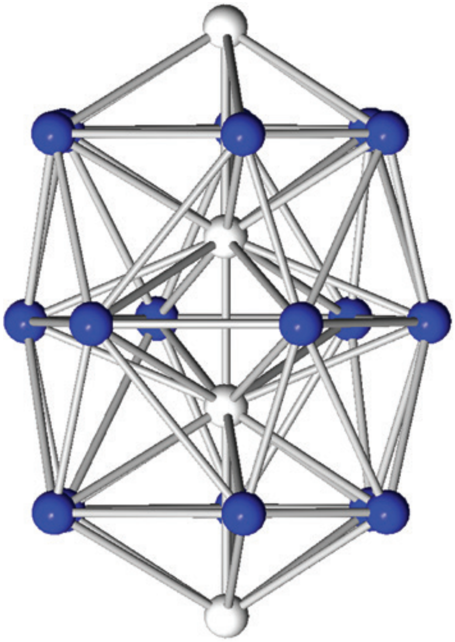

Fig. 4: Example of two interpenetrating Frank-Kasper polyhedra formed by Te atoms with coordination number 14 (central atom Te4 indicated as white sphere).

Tab. 4: Coordination numbers (CN) and distance ranges for Te atoms (Å).

Atom	CN	*d*(Te-Te)
Te1	14	$3.79 < d < 4.98$
Te2	15	$4.36 < d < 5.44$
Te3	15	$4.36 < d < 4.98$
Te4	14	$3.78 < d < 4.97$
Te5	12	$2.85 < d < 4.98$
Te6	12	$2.85 < d < 4.99$
Te7	12	$3.58 < d < 5.44$
Te8	14	$3.51 < d < 4.95$

Why was the structure of natural stützite not properly solved before?

The lack of structural information for natural stützite can be related, on the one hand, to a lack of suitable crystals and, on the other hand, to the difficulty in describing the Ag^+ electron density. If the former situation is easily understood, the latter one is more complex and should be related to the observation that the Ag^+ d^{10} element easily adopts various complex asymmetric coordinations [23]. Therefore, it is quite common to have Ag^+ in different, but very close sites. This certainly also favors the presence of strong ionic conductivity documented also for stützite [24, 25], the activation energy of the jumps from site to site being lowered by the easy density deformation. Regardless of whether there is ionic conduction or not, the structure appears to be disordered. This is exactly what was observed in all the structural investigations of natural stützite and synthetic stützite-like compounds [16, 17], independently from the cooling rates or the experimental conditions of the synthesis of such phases. All authors who have approached the stützite structure have used the "split-atom model" to deal with the disorder in their structure determination. This approach has several disadvantages and may give rise to ambiguities. As demonstrated by Bachmann and Schulz [26], the introduction in the refinement of additional positions with fractional site occupation factors does not necessarily mean that those extra positions correspond to occupied equilibrium sites. This is certainly true in the case of fast ionic conductors, for which there exists a delocalization of an ionic species over a liquid-like structure. Apart from these physically non meaningful refined positions, the simultaneous refinement of overlapping atoms with partial occupancy usually gives rise to high correlations and unstable refinements, the closer the refined positions in a disordered structure, the higher the correlations and the less stable the refinement. A solution to that problem is the use of higher order tensor elements in the expression of the structure factors (the "non harmonic approach"; [20, 27]). Indeed, initially used for true anharmonic atomic vibration, it has been shown to give an equivalent description, but with less parameters, than the split-atom model in the case of disorder with highly overlapping electron densities [28]. This alternative approach, in particular the Gram-Charlier formalism which is recommended by the IUCr Commission on Crystallographic Nomenclature [29], provides an easier convergence of the refinement, due to much lower correlations between the refined parameters. One potential drawback of the method one should be aware of, however, consists of the possible negative regions one could find in the probability density functions (*pdf*), which then indicate the inadequacy of the results. In some situations, it may then be better to use only the Gaussian approximation, even though the resulting R factors may be higher. This problem having been mastered, the non-harmonic approach has been successfully used over the past 20 years in solving numerous mineral structures, like the complex structures in the pearceite-polybasite mineral family [30–35], and it has been used here to finally decipher the complexity of the structure of the mineral stützite.

Conclusions

The crystal structure of the mineral stützite has been solved from X-ray single-crystal diffraction data. We show that the Ag cations are highly disordered, distributed along diffusion-like paths joining low-coordination preferential sites. The diffusion-like paths for some Ag atoms have been evidenced by means of a combination of a Gram-Charlier development of the atomic displacement factors and a split model. The observed disorder is strictly correlated to the ionic thermoelectric nature (mainly the intrinsic low lattice thermal conductivity) observed for these compounds [25]. Also, the different non-stoichiometry of Ag in natural and synthetic stützite-like compounds could be responsible for the stabilization of different polytypes.

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