

The crystal structure and compositional range of mckinstryite

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[Received 10 February 2010; Accepted 20 February 2010]

ABSTRACT

The previously unknown crystal structure of mckinstryite, originally described as $\text{Ag}_{1.18}\text{Cu}_{0.82}\text{S}$ or $(\text{Ag,Cu})_2\text{S}$, was solved and refined using single-crystal X-ray diffractometer data collected from a sample from the Clara mine, Black Forest (Mo- $K\alpha$ radiation, CCD area detector, $R1(F) = 3.85\%$). Mckinstryite has the refined formula $\text{Ag}_{4.92}\text{Cu}_{3.08}\text{S}_4$ or $\text{Ag}_{1.23}\text{Cu}_{0.77}\text{S}$ (idealized $\text{Ag}_5\text{Cu}_3\text{S}_4$ or $\text{Ag}_{1.25}\text{Cu}_{0.75}\text{S}$) and crystallizes in space group $Pnma$ (no. 62), with $a = 14.047(3)$ Å, $b = 7.805(2)$ Å, $c = 15.691(3)$ Å, $V = 1720.3(7)$ Å³, $Z = 8$. The structure contains five Ag, six Cu and eight S sites in the asymmetric unit. One of the Ag sites shows minor Cu-for-Ag substitution. The topology is based on flat, interrupted (010) layers of Cu and S atoms (all atoms on $y = 0.25$), in which the Cu atoms show triangular or two-coordination to S (interrupted {6,3} tiling). These layers alternate with uneven layers consisting of Ag atoms showing irregular three- to two-coordination to S. Some fairly short Ag–Cu contact distances (2.781–2.884 Å) strongly indicate that metal-metal interaction plays an important role in mckinstryite. The topology is related to that of stromeyerite ($\sim\text{AgCuS}$) which contains complete flat layers of Cu atoms triangularly coordinated to S atoms, alternating with layers of loosely packed Ag atoms.

A critical evaluation of literature data on the chemical composition and unit-cell parameters of mckinstryite confirms the presence of a small compositional range of mckinstryite which extends approximately from $\text{Ag}_{1.18}\text{Cu}_{0.82}\text{S}$ to $\text{Ag}_{1.25}\text{Cu}_{0.75}\text{S}$, with the presently studied sample being fairly Ag-rich. The accurate limits of this range at ambient temperature are still to be determined.

KEYWORDS: mckinstryite, crystal structure, single-crystal X-ray diffraction, compositional range, crystal chemistry, Ag-Cu sulphide.

Introduction

THE synthetic equivalent of the Ag-Cu sulphide mckinstryite was originally discovered as an unidentified phase (β -phase) during an X-ray diffraction study of the system Ag-Cu-S by Djurle (1958) who suggested the formula $\text{Ag}_{1.2}\text{Cu}_{0.8}\text{S}$ and reported phase transition temperatures at 97°C and 130°C. A detailed investigation of the system Ag-Cu-S by Skinner (1966), including isothermal sections at 25 and 250°C, confirmed this phase and determined its composition to be $\text{Ag}_{1.18}\text{Cu}_{0.82}\text{S}$. On heating, the phase was found to break down at $94.4^\circ\text{C} \pm 1.5^\circ\text{C}$

to a two-phase intergrowth of jalpaite (Ag_3CuS_2) and a cation-disordered hexagonal-close-packed phase of composition $\text{Ag}_{1.04}\text{Cu}_{0.96}\text{S}$. Above $139 \pm 10^\circ\text{C}$ the composition again becomes a single phase, with the formation of a cation-disordered, face-centred-cubic compound of a high-digenite type. This cubic phase, which is unquenchable, is stable up to the liquidus.

Subsequently, a natural occurrence of the β -phase ($\text{Ag}_{1.18}\text{Cu}_{0.82}\text{S}$) in a specimen from the Foster Mine, Cobalt, Ontario, was reported by Skinner *et al.* (1966) who named the phase mckinstryite. They suggested the space group $Pnma$ or $Pn2_1a$, with $a = 14.047(5)$ Å, $b = 7.803(3)$ Å, $c = 15.677(6)$ Å and 32 formula units $(\text{Ag,Cu})_2\text{S}$ in the unit cell. Later reports on additional occurrences in sulphide deposits indicated slightly variable unit-cell parameters

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DOI: 10.1180/minmag.2010.074.1.73

and Ag:Cu ratios, also reflected by small variations in reflectance properties (Robinson and Morton, 1971; Atanasov and Lavrentiev, 1973; Bergstöl and Vokes, 1974; Yarenskaya *et al.*, 1975; Šulcová and Kašpar, 1986; Pekov and Karpenko, 1996). Thus, the general formula $\text{Ag}_{1.2-x}\text{Cu}_{0.8+x}\text{S}$, where $0 \leq x \leq 0.02$ (originally suggested by Skinner *et al.*, 1966) was adopted in the recent review on the system Ag-Cu-S by Kubaschewski *et al.* (2006). In mineralogical databases and encyclopedias, the formula of mckinstryite is usually given in its simplified form $(\text{Ag,Cu})_2\text{S}$.

All reported occurrences of mckinstryite were interpreted to be the result of a low-temperature (generally below the reported phase transition at 94.4°C) genesis of either hypogene or supergene character.

Mckinstryite is one of three solid phases on the join $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}$ (at ambient temperature), all of which are known as minerals. The two neighbouring phases are jalpaite (Ag_3CuS_2 , tetragonal; Baker *et al.*, 1992; Asadov *et al.*, 2008; Trots *et al.*, 2008) and stromeyerite ($\sim\text{AgCuS}$, orthorhombic; Frueh, 1955; Baker *et al.*, 1991; Trots *et al.*, 2007). Both have been studied in some detail because of their superionic conductivity (e.g. Trots *et al.*, 2007; Skomorokhov *et al.*, 2008, and references therein).

Mckinstryite was recently identified on two different, well crystallized specimens from the famous Clara barite and fluorite mine, Black Forest, Germany. Material from one of these samples was used for a determination of the previously unknown atomic arrangement of mckinstryite. The results of the crystal-structure determination are presented in this paper, including a discussion of the stoichiometry and compositional range of the mineral (on the basis of a critical evaluation of literature data) and a comparison with related minerals.

Experimental

The mentioned mckinstryite-bearing specimen contains small (<0.2 mm), metallic-grey, euhedral prisms which show a slightly bent to worm-like distortion. Some of the crystals exhibit distorted, pseudo-tetragonal-pyramidal crystal terminations (similar to those commonly shown by natrolite crystals). Fresh fracture surfaces are black and have strong metallic lustre. The prisms are grown in a small void in white barite and are accompanied by tiny rosettes of greenish, thin

tabular crystals of a mineral assumed to belong to the beudantite-segnitite-dussertite series. Semiquantitative chemical analyses of a carbon-coated crystal by conventional energy-dispersive X-ray spectrometry in a scanning electron microscope (SEM-EDS) showed the presence of Ag, Cu and S; no other elements were detected.

X-ray diffraction

A suitable crystal of very good diffracting quality was selected for an intensity data collection with a Nonius KappaCCD single-crystal diffractometer which was equipped with a 300 µm diameter capillary-optics collimator to provide increased resolution (for details, see Table 1). The data were processed with the Nonius program suite *DENZO-SMN* and corrected for Lorentz, polarization, background and absorption effects. Observed extinctions and intensity statistics strongly suggested the *Pnma* space group, in agreement with the results of Skinner *et al.* (1966). The crystal structure was solved in space group *Pnma* by direct methods (*SHELXS-97*, Sheldrick 2008), and the positions of all atoms were located using subsequent difference-Fourier maps. A full-matrix, anisotropic least-squares refinement on F^2 (*SHELXL-97*, Sheldrick, 2008; see Table 1) led to a final $R1(F)$ of 3.85%. Prior to the final refinement step, the coordinate set was standardized using the programme *STRUCTURE TIDY* (Gelato and Parthé, 1987).

The final atomic positions and displacement parameters of mckinstryite from the Clara mine are given in Table 2. Selected bond lengths and calculated bond valences are listed in Table 3. A CIF file and a list of observed and calculated structure factors have been deposited with the Principal Editor of *Mineralogical Magazine* and are available from www.minersoc.org/pages/e_journals/dep_mat_mm.html.

Results and Discussion

Structure and compositional range

The structure determination demonstrates that the asymmetric unit of mckinstryite from the Clara mine contains five Ag, six Cu and eight S sites. All Ag sites are on general positions, whereas all Cu and S sites are on special positions ($y = 0.25$). Occupancy refinements demonstrated that all Cu sites are fully occupied by Cu (refined occupancies for the atoms Cu(1)–Cu(6) are 1.00, 1.01, 1.00, 1.00, 1.00 and 0.99), whereas one of the five

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TABLE 1. Crystal data, data collection information and refinement details for mckinstryite from the Clara mine, Black Forest.

Mckinstryite	
Crystal data	
Formula	Ag _{4.92} Cu _{3.08} S ₄ (~Ag ₅ Cu ₃ S ₄)
Space group	<i>Pnma</i> (no. 62)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	14.047(3), 7.805(2), 15.691(3)
<i>V</i> (Å ³), <i>Z</i>	1720.3(7) Å ³ , 8
μ (mm ⁻¹), ρ_{calc} (g·cm ⁻³)	19.30, 6.601
Absorption correction	multi-scan (Otwinowski <i>et al.</i> , 2003)
Crystal dimensions (mm)	0.07 × 0.07 × 0.17
Data collection and refinement	
Diffractometer	Nonius KappaCCD system
<i>T</i> (K); λ (Mo- <i>K</i> α) (Å)	293; 0.71073
Detector distance (mm)	34
Rotation axes; width (°)	ϕ ω ; 1.5
Total no. of frames	728
Collection time/frame (s)	50
$2\theta_{\text{max}}$ (°)	69.94
<i>h</i> , <i>k</i> , <i>l</i> ranges	−22 → 22, −12 → 12, −25 → 25
Total refls. measured	7337
Unique reflections	4003 (<i>R</i> _{int} = 2.11 %)
<i>R</i> 1(<i>F</i>), <i>wR</i> 2(<i>F</i> _o ²) [*]	3.85%, 10.87
'Observed' reflections	2684 [<i>F</i> _o > 4σ(<i>F</i> _o)]
No. of refined parameters	132
Extinct. coefficient	0.00102(6)
GoF	1.047
(Δ/σ) _{max}	0.000
Δρ _{min} , Δρ _{max} (e Å ⁻³)	−2.28, 2.27**

Unit-cell parameters were refined from 4254 reflections.

Scattering factors for neutral atoms were employed in the refinement.

* $w = 1/[\sigma^2(F_o^2) + (0.047P)^2 + 8P]$; $P = ([\text{max of } (0 \text{ or } F_o^2)] + 2F_o^2)/3$.

** Largest peak at 0.66 Å from Cu(3), deepest hole at 0.74 Å from Ag(4).

Ag sites, Ag(3), contains minor Cu (refined occupancy: Ag_{0.925(6)}Cu_{0.075(6)}). The remaining Ag sites, Ag(1), Ag(2), Ag(4) and Ag(5), have refined occupancies of 1.00, 0.99, 1.01 and 1.00. Thus, the studied crystal has the formula Ag_{4.92}Cu_{3.08}S₄ or Ag_{1.23}Cu_{0.77}S. This could be idealized to Ag₅Cu₃S₄ or Ag_{1.25}Cu_{0.75}S. Both refined and idealized compositions are richer in Ag than that of the type material (Ag_{1.18}Cu_{0.82}S; Skinner *et al.*, 1966) and fairly Ag-rich by comparison to other published analyses of mckinstryite (Table 4, compilation of critically evaluated unit-cell and chemical data). Samples having a similarly Ag-rich composition are those from the Sedmochislenitsi deposit (Ag_{1.27}Cu_{0.76}As_{0.01}S_{0.97}; Atanasov and

Lavrentiev, 1973) and the Sarbai deposit (Ag_{1.22}Cu_{0.81}S_{0.98}; Pekov and Karpenko, 1996). The sample having the smallest Ag content is that of the synthetic mckinstryite analysed by Skinner (1966) (Ag_{1.18}Cu_{0.82}S), which equals that of the type material (Skinner *et al.*, 1966).

A comparison of the unit-cell parameters of the Clara sample (*a* = 14.047(3) Å, *b* = 7.805(2) Å, *c* = 15.691(3) Å, *V* = 1720.3(7) Å³) and the type material (*a* = 14.047(5) Å, *b* = 7.803(3) Å, *c* = 15.677(6) Å, *V* = 1717.8(8) Å³; Skinner, 1966) shows that the increased Ag content of the Clara sample is reflected by a slightly increased length of the *c* axis (both *a* and *b* axes are of identical lengths within error limits), i.e. corresponding to the rows of Ag atoms 'arranged' along the *c* axis. The unit-

TABLE 2. Fractional atomic coordinates and displacement parameters (in Å²) for mckinstyrite from the Clara mine (s.u.s in parentheses).

	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ag(1)	0.09176(4)	0.54813(5)	0.09008(3)	0.04316(13)	0.0593(3)	0.0242(2)	0.0459(3)	0.00332(17)	0.0053(2)	-0.00311(19)
Ag(2)	0.14746(4)	0.04547(5)	0.28118(3)	0.04047(13)	0.0496(3)	0.0247(2)	0.0471(3)	-0.00727(17)	0.0079(2)	-0.00009(17)
Ag(3)*	0.14968(4)	0.04447(5)	0.47155(3)	0.03882(18)	0.0426(3)	0.0256(2)	0.0482(3)	0.00663(18)	-0.0078(2)	0.00121(17)
Ag(4)	0.36551(5)	0.05378(6)	0.38286(4)	0.05449(17)	0.0630(4)	0.0245(2)	0.0759(4)	-0.0017(2)	0.0093(3)	0.0065(2)
Ag(5)	0.40752(4)	0.03828(6)	0.17491(4)	0.04716(15)	0.0453(3)	0.0288(2)	0.0674(3)	-0.0119(2)	0.0084(2)	0.00221(19)
Cu(1)	0.20523(6)	0.25	0.62233(6)	0.02783(19)	0.0179(4)	0.0327(5)	0.0329(4)	0	-0.0017(3)	0
Cu(2)	0.21109(6)	0.25	0.13139(6)	0.0289(2)	0.0220(4)	0.0327(5)	0.0321(5)	0	0.0023(3)	0
Cu(3)	0.25446(8)	0.25	0.87318(6)	0.0311(2)	0.0439(5)	0.0277(4)	0.0216(4)	0	0.0007(4)	0
Cu(4)	0.46383(7)	0.25	0.00358(6)	0.0304(2)	0.0208(4)	0.0353(5)	0.0350(5)	0	-0.0011(3)	0
Cu(5)	0.46884(6)	0.25	0.74449(6)	0.02609(18)	0.0203(4)	0.0269(4)	0.0310(4)	0	-0.0017(3)	0
Cu(6)	0.55523(8)	0.25	0.50127(6)	0.0330(2)	0.0428(6)	0.0331(5)	0.0230(4)	0	0.0056(4)	0
S(1)	0.04573(11)	0.25	0.62453(10)	0.0206(3)	0.0159(6)	0.0265(7)	0.0193(6)	0	-0.0001(5)	0
S(2)	0.30802(11)	0.25	0.73871(10)	0.0199(3)	0.0155(6)	0.0262(7)	0.0179(6)	0	-0.0016(5)	0
S(3)	0.30710(13)	0.25	0.50522(11)	0.0286(4)	0.0215(8)	0.0431(10)	0.0212(7)	0	0.0019(6)	0
S(4)	0.04782(11)	0.25	0.13756(10)	0.0223(3)	0.0176(7)	0.0267(8)	0.0226(7)	0	0.0004(6)	0
S(5)	0.30319(11)	0.25	0.00898(10)	0.0218(3)	0.0144(6)	0.0318(8)	0.0191(7)	0	0.0013(5)	0
S(6)	0.30764(13)	0.25	0.25144(11)	0.0269(3)	0.0212(8)	0.0342(9)	0.0254(8)	0	-0.0007(6)	0
S(7)	0.58011(11)	0.25	0.63763(11)	0.0219(3)	0.0176(7)	0.0231(7)	0.0250(7)	0	0.0038(6)	0
S(8)	0.05990(13)	0.25	0.37751(11)	0.0261(3)	0.0241(8)	0.0292(8)	0.0251(8)	0	0.0045(6)	0

* Refined occupancy: Ag_{0.925(6)}Cu_{0.075(6)}. U_{eq} defined according to Fischer and Tillmanns (1988).

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TABLE 3. Selected interatomic distances (Å) and calculated bond valences (v.u.) in mckinstryite from the Clara mine.

Ag(1)–S(3)	2.5047(15)	0.353	Cu(1)–S(1)	2.2407(18)	0.396
S(4)	2.5200(9)	<u>0.338</u>	S(2)	2.3280(18)	0.313
<Ag(1)–S>	2.512*	0.69 v.u.*	S(3)	2.3290(19)	<u>0.312</u>
			<Cu(1)–S>	2.299	1.02 v.u.
Ag(2)–S(2)	2.4806(9)	0.376			
S(8)	2.5191(14)	0.339	Cu(2)–S(4)	2.2955(19)	0.342
S(6)	2.7980(16)	<u>0.160</u>	S(5)	2.3158(18)	0.323
<Ag(2)–S>	2.599	0.88 v.u.	S(6)	2.321(2)	<u>0.319</u>
			<Cu(2)–S>	2.311	0.98 v.u.
Ag(3)–S(5)	2.4628(9)	0.395			
S(8)	2.5181(15)	0.340	Cu(3)–S(5)	2.2382(18)	0.399
S(3)	2.7825(16)	<u>0.166</u>	S(2)	2.2400(18)	0.397
<Ag(3)–S>	2.588	0.90 v.u.	S(7)	2.455(2)	<u>0.222</u>
			<Cu(3)–S>	2.311	1.02 v.u.
Ag(4)–S(7)	2.5117(9)	0.346			
S(3)	2.5895(15)	0.280	Cu(4)–S(5)	2.2581(18)	0.378
S(6)	2.6942(16)	<u>0.211</u>	S(8)	2.303(2)	0.335
<Ag(4)–S>	2.598	0.84 v.u.	S(1)	2.3160(19)	<u>0.323</u>
			<Cu(4)–S>	2.292	1.04 v.u.
Ag(5)–S(1)	2.4736(9)	0.384			
S(6)	2.4781(15)	0.379	Cu(5)–S(2)	2.2610(18)	0.375
S(8)	2.8265(17)	<u>0.148</u>	S(7)	2.2923(19)	0.344
<Ag(5)–S>	2.593	0.91 v.u.	S(1)	2.3218(18)	<u>0.318</u>
			<Cu(5)–S>	2.292	1.04 v.u.
Ag(1)–Cu(6)	2.7806(8)		Cu(6)–S(7)	2.168(2)	0.482
Ag(2)–Cu(5)	2.8842(9)		S(4)	2.1808(19)	<u>0.466</u>
Ag(3)–Cu(4)	2.8421(9)		<Cu(6)–S>	2.174	0.95 v.u.
Ag(5)–Cu(1)	2.8725(9)				

* A further, very long Ag(1)–S(7) distance (2.98 Å) is not considered a bonding distance, although it would increase the bond-valence sum by about 0.1 v.u.

Bond-valence sums (v.u.) for the S atoms S(1)–S(8) are as follows: 1.81 S(1); 1.84 S(2); 1.91 S(3); 1.48 S(4) [see text for discussion]; 1.89 S(5); 1.82 S(6); 1.74 S(7); 1.99 S(8).

Bond-valence parameters used are from Brown and Altermatt (1985) and were calculated using *VALENCE* (Brown, 1996; updated values from www.ccp14.ac.uk/ccp/web-mirrors/i_d_brown); sum values are derived from unrounded bond-valence contributions.

cell volume is thus only slightly larger. The sample from the Sarbai deposit, which was described by Pekov and Karpenko (1996), has an even larger unit-cell volume (1722.6 Å³), but a composition slightly poorer in Ag (Ag_{1.22}Cu_{0.81}S_{0.98}).

The data in Table 4 further suggest that the compositional range of mckinstryite at ambient temperature extends approximately from Ag_{1.18}Cu_{0.82}S to Ag_{1.25}Cu_{0.75}S. An accurate check on the compositional range of the mineral has not yet been determined experimentally. It is, however, assumed to be small (Skinner, 1966;

Kubaschewski, 2006), and similar to that of stromeyerite, for which several independent studies consistently gave the formula Ag_{1–x}Cu_{1+x}S, $x = 0–0.1$ (Frueh, 1955; Suhr, 1955; Djurle, 1958; Skinner, 1966; Skinner *et al.*, 1966; Rojković, 1973; Bergstöl and Vokes, 1974; Baker *et al.*, 1991; Pekov and Karpenko, 1996; Kubaschewski *et al.*, 2006; Asadov *et al.*, 2008; Tokuhara *et al.*, 2009). This formula is, on average, slightly richer in Cu and poorer in Ag than the ‘end-member’ formula AgCuS usually given in mineral databases and encyclopedias.

TABLE 4. Comparison of chemical analyses and crystal data for natural and synthetic mckinstryite.

Locality	Formula	Space group	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	Ref.
Synth. (β-phase)	Ag _{1.2} Cu _{0.8} S						Djurle (1958)
Synth. (β-phase)	Ag _{1.18} Cu _{0.82} S						Skinner (1966)
Foster mine (type locality)	Ag _{1.18} Cu _{0.82} S	<i>Pnma</i> or <i>Pn2₁a</i>	14.043(5)	7.803(3)	15.677(6)	1717.8(8)	Skinner <i>et al.</i> (1966)
Echo Bay mine	variable, Ag _{1.28} Cu _{0.72} S _{0.91} to Ag _{1.21} Cu _{0.79} S _{0.93} *	<i>P***</i>	13.962(1)	7.755(2)	15.675(2)	1697.2(3)	Robinson and Morton (1971)
Sedmochislensitsi deposit	Ag _{1.27} Cu _{0.76} S _{0.97} As _{0.01}						Atanasov and Lavrentiev (1973)
Great Bear Lake	Ag _{1.18} Cu _{0.82} S**						Rojkovič (1973)
Godejord deposit	Ag _{1.19} Cu _{0.77} S						Bergstöl and Vokes (1974)
Tortkuduk deposit	Ag _{1.20} Cu _{0.86} S _{0.92} As _{0.01} ***						Yarenskaya <i>et al.</i> (1975)
Vrančice	Ag _{1.20} Cu _{0.79} S _{1.00}						Šulcová and Kašpar (1986)
Sarbai deposit	Ag _{1.22} Cu _{0.81} S _{0.98}	<i>P***</i>	14.066(1)	7.790(1)	15.721(1)	1722.6	Pekov and Karpenko (1996)
Clara mine	Ag _{1.23} Cu _{0.77} S (idealized Ag _{1.25} Cu _{0.75} S)	<i>Pnma</i>	14.047(3)	7.805(2)	15.691(3)	1720.3(7)	This work

If necessary, unit cells have been transformed to conform to the standard *Pnma* space-group setting.

* These analyses of Robinson and Morton (1971) are considered unreliable since normalization on *S* = 1 gives unreasonably Ag-rich compositions from Ag_{1.41}Cu_{0.79}S to Ag_{1.30}Cu_{0.85}S. See also discussion in Bergstöl and Vokes (1974), who observed instability of both mckinstryite and, to a lesser extent, stromeyerite and probable loss of sulphur under the electron beam during EPMA; reliable analytical results were only obtained with reduced acceleration voltages and probe currents, and a defocused beam.

** The analysis of Rojkovič (1973) is based on Ag+Cu = 2, 'due to small leak of S'.

*** These analyses of Yarenskaya *et al.* (1975) are considered unreliable since the *S* content deviates strongly from the ideal formula.

Connectivity and coordination environments

The topology of mckinstryite (Figs 1–4) is based on two different, alternating atomic layers. A flat (010) layer contains Cu and S atoms (all atoms on $y = 0.25$); the Cu atoms show triangular or two-coordination by S (Figs 2, 3). This layer may be described as a strongly interrupted {6,3} tiling or honeycomb lattice. Part of the interruption is caused by the Cu(1) atom that shows two-coordination, unlike the remaining five Cu atoms which all show triangular coordination (Table 3). The other reason for the interruption are ‘missing’ Cu atoms within the tiling. Both features result in ‘zig-zag’ ribbons extending parallel to [100] which are not connected to each other (Fig. 3). The ribbon consists of four weakly distorted hexagons and one strongly distorted hexagon – the angle S(7)–Cu(6)–S(4) characterizing the two-coordinated Cu(6) atom is $173.46(8)^\circ$, and thus strongly deviates from the ideal 120° angle of a {6,3} tiling.

The second, uneven layer consists of Ag atoms showing irregular three- to two-coordination by S atoms belonging to the adjacent Cu–S layers

(Figs 2, 4). This bonding scheme results in ‘zig-zag’ chains containing one distorted hexagon or six-ring [formed by Ag(2), Ag(3), Ag(4), S(3), S(6) and S(8)] and side ‘branches’ extending approximately parallel to $\langle 101 \rangle$ [the bent connection S(3)–Ag(1)–S(4) of the two-coordinated Ag(1) atom].

If one superimposes the two alternating layers, one recognizes that the Ag(2), Ag(3), Ag(4) and Ag(5) atoms are located above and below the open areas (‘missing’ Cu atoms) between the unconnected ribbons in the interrupted Cu–S layer (Figs 1, 3). In other words, these Ag atoms connect the ribbons *via* Ag–S bonds. The positions of the S atoms in the structure are those of a highly distorted hexagonal-close-packed anion array.

The S atoms are all five-coordinated by a combination of Ag and Cu atoms (within 2.90 Å), except S(4) which is four-coordinated in a highly asymmetric, pyramidal way by two Ag(1), one Cu(2) and one Cu(6) atom [four further Ag neighbours are at $3.00 \text{ Å} (\times 2)$ and $3.10 \text{ Å} (\times 2)$], and the three atoms S(3), S(6) and S(8) which are

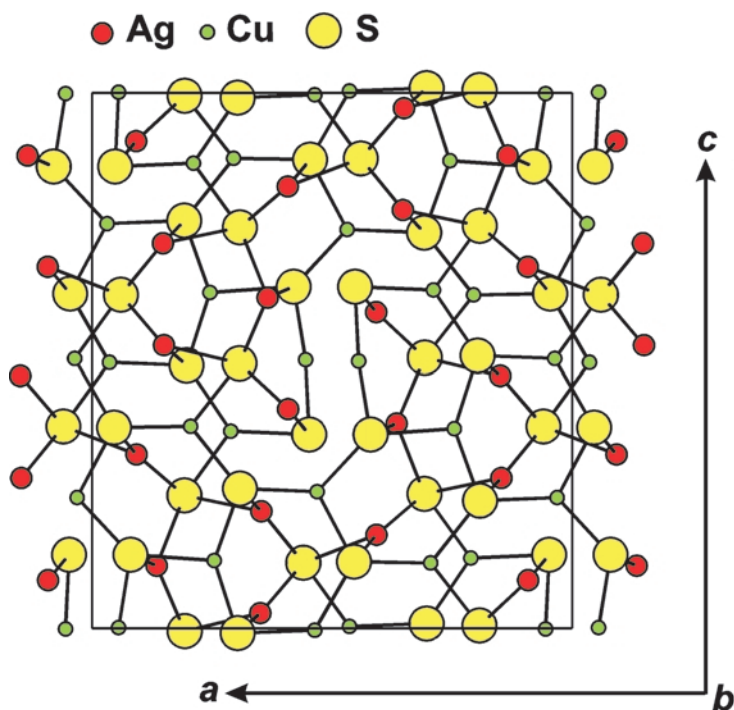


FIG. 1. View of the connectivity in mckinstryite along the b axis, perpendicular to the Cu–S and Ag layers. Drawings were produced with *ATOMS* (Shape Software, 1999).

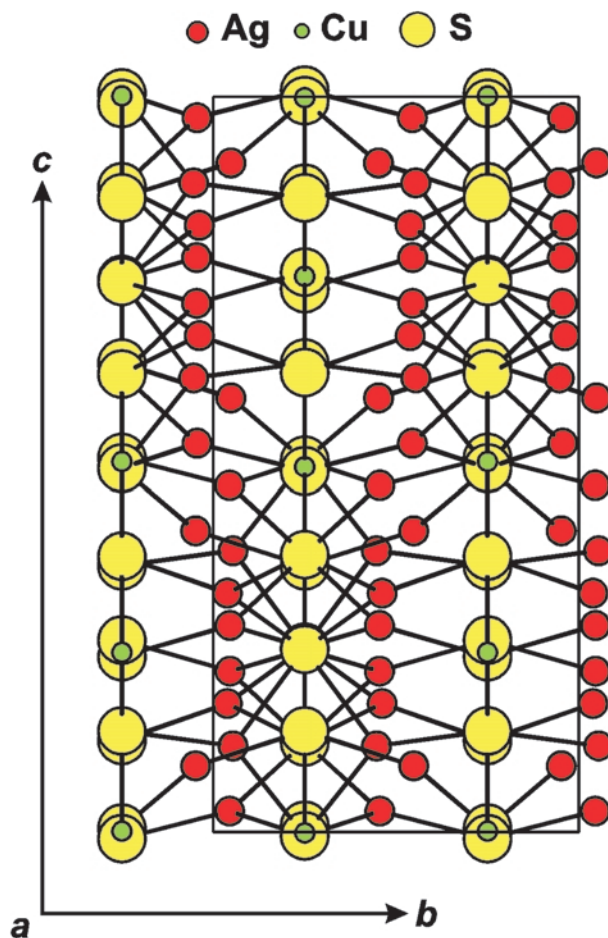


FIG. 2. The layered character of the mckinstryite structure is evident in this view along the a axis. Note that all Cu and S atoms are on special positions ($y = 0.25$ and their symmetry equivalents at $y = 0.75$).

all seven-coordinated. Those five Cu atoms, which show triangular coordination, are characterized by very similar average Cu–S bond lengths (range: 2.292–2.311 Å; Table 3). The four three-coordinated Ag atoms have average Ag–S bond distances which are equally within a very narrow range (2.588–2.599 Å).

The atomic arrangement is furthermore characterized by some fairly short Ag–Cu contact distances (2.781–2.884 Å, Table 3, bottom left) which strongly indicate that metal-metal interaction plays an important role in mckinstryite. These contact distances are shorter than several of the short metal–S bond distances (cf. Table 3), and also shorter than those in stromeyerite (minimum contact distances at ambient temp-

erature: 2.875(7) and 2.881(7) Å; Baker *et al.*, 1991) and jalpaite (2.974(5) Å; Baker *et al.*, 1992). Some of the Ag–Ag distances in mckinstryite are also shorter (e.g. Ag(2)–Ag(3) = 2.9872(9) Å; Ag(4)–Ag(4)' = 3.0630(13) Å) than those in stromeyerite (3.88(2) Å) and jalpaite (shortest value: 3.124(2) Å). The Ag atoms in mckinstryite are expected to move easily within their uneven (010) layers, as is also indirectly suggested by the discus-like shape of the anisotropic displacement ellipsoids which are slightly flattened approximately parallel to the (010) plane. Silver diffusion in synthetic $\text{Ag}_{1.2}\text{Cu}_{0.8}\text{S}$ was studied by Schmidt and Sagua (1999). High mobility of Ag and Cu atoms in all three known Ag–Cu sulphides is also demon-

CRYSTAL STRUCTURE OF MCKINSTRYITE

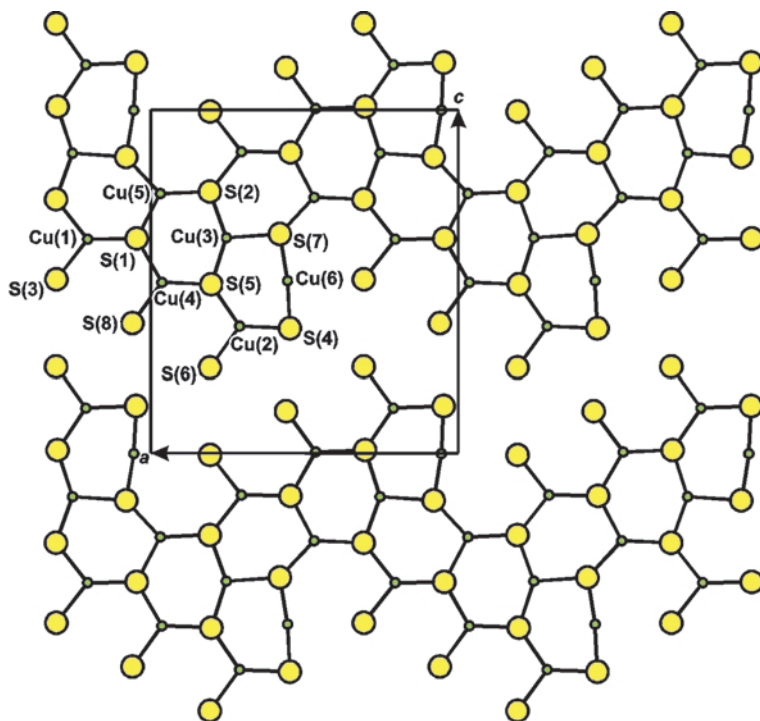


FIG. 3. View perpendicular to the planar, interrupted Cu-S (010) layer in mckinstryite. Note the two-coordinated Cu(6) atom causing the interruption within the unconnected ribbons extending parallel to the *a* axis.

strated by the fact that phase equilibria along the join $\text{Ag}_2\text{S}-\text{Cu}_2\text{S}$ are very rapidly attained $<100^\circ\text{C}$ and even at room temperature; none of the high-temperature phases are quenchable (Skinner, 1966).

The calculated bond-valence sums for the Cu atoms (Table 3) are close to the formal valence, while those for the Ag atoms are always lower – the three-coordinated Ag atoms have sums between 0.84 and 0.91 v.u., and the two-coordinated Ag(1) atom is characterized by a sum of only 0.69 v.u. (which would be only slightly increased to about 0.8 v.u., if the very long Ag(1)–S(7) distance (2.98 Å) were to be considered a bonding distance). However, the Ag(1) atom also shows the shortest Ag–Cu distance (2.781 Å) and is therefore assumed to gain bond-valence contributions *via* metal-metal interaction. Furthermore, the bond-valence parameters might not be flexible enough to account completely for a twofold coordination.

The calculated bond-valence sums for the S atoms (Table 3, bottom) range between 1.74 and 1.99 v.u., if the ‘anomalously’ low value for S(4) of 1.48 v.u. is neglected. This low value would,

however, increase to a more reasonable value of 1.81 v.u. if four additional, very long distances to Ag atoms of the highly asymmetrically coordinated S(4) atom (see above) were taken into account. The fairly low value of 1.74 v.u. for the S(7) atom would also increase to 1.94 v.u. if the contributions of two very long bonds to the Ag(1) at 2.98 Å ($\times 2$) were to be added to the bond-valence sum of S(7).

Relation to other species

The topology of mckinstryite is related to that of stromeyerite ($\sim\text{AgCuS}$) which contains flat (001) layers of triangularly coordinated Cu and S atoms (i.e. a fairly regular {6,3} tiling), alternating with layers of loosely packed face-centred Ag atoms. The latter are linearly two-coordinated by S atoms from a Cu-S layer above and below. Skinner *et al.* (1966) noted an apparent dimensional relationship between the cell of mckinstryite and that of stromeyerite: $a_{\text{mckin}} \sim 4d(110)_{\text{strom}}$, $c_{\text{mckin}} = d(130)_{\text{strom}}$, $b_{\text{mckin}} \sim 2c_{\text{strom}}$. This relationship is confirmed by the present study; the lengthwise

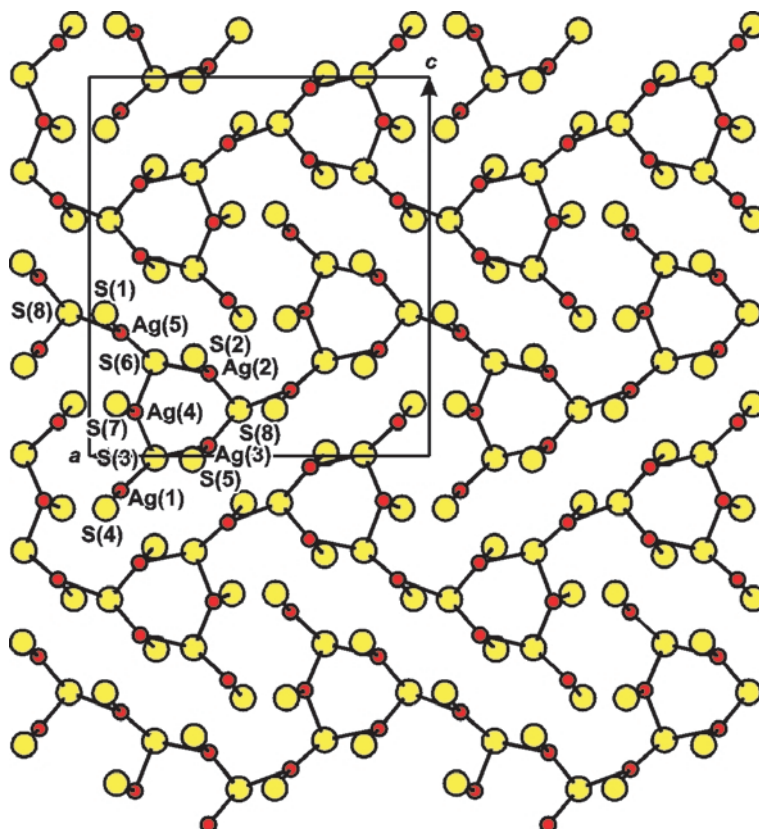


FIG. 4. View perpendicular to the uneven layer containing the Ag atoms and their S ligands in mckinstryite (based on a cut-off maximum Ag–S bond distance of 2.9 Å). The connectivity within this layer results in branched ‘zig-zag’ chains containing one distorted six-ring (see text). Note the two-coordinated Ag(1) atom.

similar axial directions are along rows of S/Cu atoms within the Cu–S layers. They indirectly reflect the similarity of the Cu–S layers and their role in the structures of the two minerals. Neighbouring Cu–S layers in mckinstryite are 3.903 Å apart, while in stromeyerite their distance is 3.984 Å.

The anisotropic displacement parameters of the Ag atoms in mckinstryite are larger and more anisotropic than those of the Cu and S atoms. The same structural feature was also observed for stromeyerite (Baker *et al.*, 1991). Although no anisotropic displacement parameters were obtained for jalpaite, the Ag atoms in it show isotropic displacement parameters which are about 3–4 times larger than those of the Cu atoms (Baker *et al.*, 1992).

The existence of selenide analogues of both stromeyerite (eucairite, AgCuSe ; Frueh *et al.*,

1957) and jalpaite (selenojalpaite, Ag_3CuSe_2 ; Bindi and Pratesi, 2005) might suggest that a selenide analogue of mckinstryite could also exist. However, none of the published studies of the system Ag_2Se – Cu_2Se (e.g. Borchert and Patzak, 1955; Frueh *et al.*, 1957; Schäfer, 1995) has indicated the presence of any compound with a stoichiometry similar to $\text{Ag}_5\text{Cu}_3\text{Se}_4$ or $\sim\text{Ag}_{1.2}\text{Cu}_{0.8}\text{Se}$. As to the author’s knowledge, no attempt has been made so far to study the extent of the solid-solution range between mckinstryite and its hypothetical selenide analogue in detail.

Acknowledgements

The author thanks Mr Siegfried Schuster of Vienna, Austria, for providing the mckinstryite-bearing sample on loan. Igor Pekov is thanked for

making a copy of his 1996 article available. The article benefited from quick and constructive reviews by Luca Bindi and an anonymous referee, and editorial assistance by Mark Welch. Emeritus Prof. Dr. Ekkehart Tillmanns is thanked for providing access to the X-ray diffraction facility in the Institut für Mineralogie und Kristallographie at the Universität Wien, Austria.

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