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Crystal structure of sternbergite, $AgFe_2S_3$

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With 2 figures and 3 tables in the text

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Abstract: The crystal structure of sternbergite, $AgFe_2S_3$, [a = 6.615(2), b = 11.639(4), c = 12.693(4) Å; space group: Ccmb-D_{2h}^{18}; Z = 8] has been determined from single crystal X-ray data and was refined to R = 0.078 for 449 reflections. The structure contains Fe_2S_3 layers parallel to (001) built up by edge sharing FeS_4 tetrahedra [Fe–S: 2.24(1) Å to 2.31(1) Å]. These layers are linked parallel to c by Ag atoms, with the Ag in a distorted tetrahedral coordination [Ag–S: 2.48(1) Å, 2.52(1) Å, and 2.63(1) Å, 2×]. The angle S–Ag–S between the two shortest Ag–S bonds is 138.6°, the other five angles vary from 99.4° to 105.6°, indicating a tendency towards a linear [2] coordination, as characteristic for a Ag(I) atom.

Key words: Crystal structure, crystal chemistry, $AgFe_2S_3$ structure, sternbergite.

Introduction

The first description of the mineral sternbergite from Jáchymov, Czechoslovakia, was given by HAIDINGER (1828) and a detailed investigation of the morphology was performed by PEACOCK (1936). By the means of single crystal X-ray work on sternbergite, two different extinction rules and therefore two different holohedral space groups resp. their hemihedral subgroups were published: Ccmm-D_{2h}^{17} by BUERGER (1937) and Cmma-D_{2h}^{21} by PEACOCK (1942). The lattice constants, given by these authors, are equal within limits of error (cf. Table 1). To get an information about the symmetry and the crystal structure of sternbergite, the present X-ray investigations were performed.

A crystal fragment of a specimen of sternbergite from the type locality Jáchymov, Czechoslovakia (HAIDINGER, 1828) from the collection of the "Landesmuseum Joanneum, Graz" (Inv. Nr. 6202, year of acquisition 1862) was used for the initial structure determination. The structure refinement was carried out on a second specimen from Měděnec, Krušné hory Mts., Czechoslovakia. Within investigations of the mineralisation of the polymetallic veins of this skarn deposit, and especially of the "Silber Kies" minerals (cf. RAMDOHR, 1955), by ŠREIN et al. (1986) crystal of sternbergite, suitable for single crystal X-ray work, were isolated.

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Structure determination

For the X-ray data collection of a preliminary structure determination a crystal chip from Jáchymov was used. The structure type was found by direct methods and difference Fourier summations. Due to the fact, that the used crystal showed extremely broad X-ray peaks (20° in ω on Weissenberg films, CuKα radiation) the expected agreement between observed and calculated structure factors was very bad ($R \sim 20\,\%$). To obtain a crystal more suitable for X-ray work – to support the structure type – a cluster of crystals, formed by sternbergite and argentopyrite, from Mědĕnec was investigated in detail. At least a crystal out of a range of about fourty individuals was found more suitable for structure refinement than the first one. The results of this refinement are described in detail.

The accurate 2ϑ values for refinement of the lattice parameters (47 reflections) as well as the X-ray intensity data of sternbergite were collected with a Stoe four-circle diffractometer AED 2 (for details cf. Table 1). The intensities were corrected for absorption (empirical ψ scans of three reflections, min. and max. transmission factors 0.35 and 0.37) as well as for Lorentz and polarization effects. The atomic parameters obtained from the first structure determination were used in the starting set of the refinement.

The structure parameters for all atoms were fit by least squares techniques. Complex neutral atomic scattering functions were used (International Tables 1974). A correction for extinction was found to be neglectible. The results are listed in Table 2. Some selected interatomic distances and bond angles are given in Table 3.

The reasons for the unsatisfactory accuracy even for the structure refinement was the poor quality and the small size of the available crystal fragment of sternbergite. Fig. 3 in the article written by Šrein et al. (1986) gives an

Table 1. Summary of crystal data, data of intensity measurements and crystal structure refinement for sternbergite.

a = 6.615(2) [6.61^{I} 6.62^{II}] Å	Stoe four-circle diffractometer
b = 11.639(4) [11.64^{I} 11.58^{II}]Å	program system STRUCSY on an ECLIPSE S 140
c = 12.693(4) [12.67^{I} 12.65^{II}] Å	crystal dimension: $0.12 \times 0.04 \times 0.04$ mm^3
space group: Ccmb-D_{2h}^{18}	graphite-monochromatized MoKα radiation
Z = 8 {$AgFe_2S_3$}	2 θ/ω-scan mode with a step width of 0.03°
ϱobs^{III} = 4.101 – 4.215 g · cm^{-3}	steps/reflection: 80 + (α_1, α_2) splitting
ϱcalc = 4.28 g · cm^{-3}	time/step: 0.5 to 3.0 s
μMoKα ~ 103 cm^{-1}	range of data: $2° < 2\theta < 50°$
no of variables: 31	measured reflections: 1050 (± h k l)
R/Rw = 0.078/0.052	independent reflections: 449
w = $[\sigma(Fo)]^{-2}$	reflections with $Fo > 2\sigma_{Fo}$: 314

I: Buerger (1937), II: Peacock (1942), III: Dana & Dana (1946).

Table 2. Atomic parameters for sternbergite. Space group: Ccmb-D_{2h}^{18}. The equivalent positions are: (0, 0, 0; ½, ½, 0) + (x, y, z; x, $\bar{y}$, z; ½−x, y, ½+z; ½−x, $\bar{y}$, ½+z); (e.s.d.'s in parentheses).
ATF [pm^2] = $\exp\left(-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij} h_i h_j a_i^x a_j^x\right)$.

atom	x/a	y/b	z/c
Ag	0.8531(4)	0.0	0.6996(2)
Fe	0.8335(5)	0.3351(2)	0.5635(2)
S(1)	0.6952(14)	0.0	0.8800(8)
S(2)	0.6658(8)	0.1786(5)	0.6179(4)

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ag	283(15)	248(15)	596(18)	0	83(16)	0
Fe	186(15)	87(15)	261(15)	10(14)	17(14)	4(16)
S(1)	323(56)	99(44)	440(55)	0	−89(42)	0
S(2)	224(26)	142(30)	340(30)	−41(39)	−8(29)	41(25)

Table 3. Selected interatomic distances (Å) and bond angles (°) for sternbergite (e.s.d.'s in parentheses). ([a]) Common edges of two Fe-S_4 tetrahedra, ([b]) Fe-Fe distances within one Fe_2S_3 layer.

Ag −	S(1)	= 2.52(1)	S(1)	− S(1')	4.67(2)	138.6(7)
	S(1')	= 2.48(1)		− S(2)	3.93(1)	99.4(2) 2 ×
	S(2)	= 2.63(1) 2 ×	S(1')	− S(2)	4.07(1)	105.6(2) 2 ×
			S(2)	− S(2')	4.16(1)	104.3(3)
Fe −	S(1)	= 2.24(1)	S(1)	− S(2)	3.75(1)	113.2(2)
	S(2)	= 2.24(1)		− S(2')	3.78(1)	112.3(3)
	S(2')	= 2.31(1)		− S(2")	3.74(1)	110.6(3)
	S(2")	= 2.31(1)	S(2)	− S(2')	3.60(1)([a])	104.6(3)
				− S(2")	3.70(1)	108.8(3)
			S(2')	− S(2")	3.71(1)([a])	107.0(3)
S(1) −	Ag	= 2.52(1)	Ag	− Ag'	3.55(1)	90.5(5)
	Ag'	= 2.48(1)		− Fe	3.57(1)	97.0(3) 2 ×
	Fe	= 2.24(1) 2 ×	Ag'	− Fe	4.10(1)	120.2(2) 2 ×
			Fe	− Fe'	3.84(1)	117.6(4)
S(2) −	Ag	= 2.63(1)	Ag	− Fe	4.27(1)	122.0(2)
	Fe	= 2.24(1)		− Fe'	4.05(1)	109.7(2)
	Fe'	= 2.31(1)		− Fe"	4.30(1)	120.7(2)
	Fe"	= 2.31(1)	Fe	− Fe'	2.78(1)	75.4(3)
				− Fe"	3.86(1)	115.8(3)
			Fe'	− Fe"	2.73(1)	72.5(3)

Fe − Fe' = 2.73(1)([b])
− Fe" = 2.78(1)([b]).

impression of the difficulties to find a crystal fragment suitable for structure determination.

Discussion

The Ag atom in the structure of sternbergite has a clear four-coordination by S atoms (cf. Table 3). The two Ag−S(1) bonds are shorter by 6.06 and 4.55 %

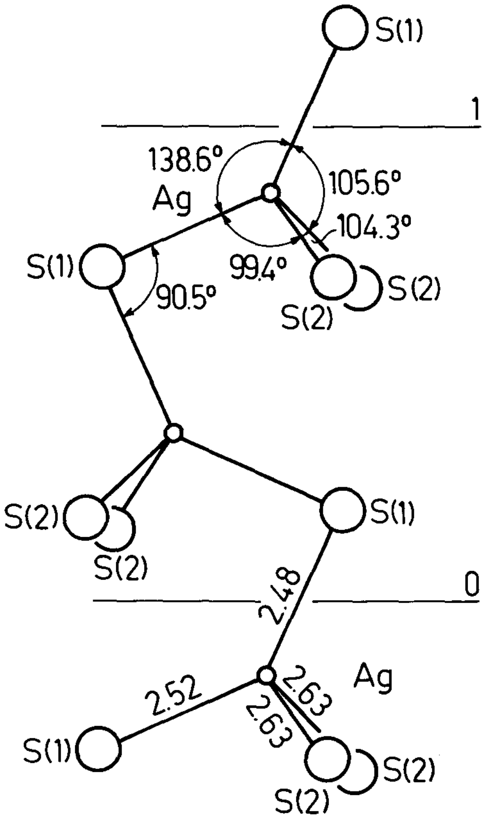

Fig. 1. AgS_4 polyeder connected over common S atom corners to a chain parallel [100]. Distances are given in Å, angles in °. The drawing is inclined to the direction [100] by about 5°.

than the two Ag–S(2) bonds; the angle S(1)–Ag–S(1') is 138.6°. Therefore the coordination polyhedron around the Ag atom can best be described as a distorted tetrahedron with a tendency towards a linear [2] coordination. This crystal chemical behaviour is typical for monovalent Ag atoms and occurs in a lot of crystal structures (cf. FRUEH, 1958, 1969; WELLS, 1975). The AgS_4 polyhedra are connected over common S atom corners to chains parallel [100]. One of these chains is drawn in Fig. 1.

The Fe atom is tetrahedrally coordinated to S atoms with Fe–S distances ranging from 2.24 to 2.31 Å. These values are in good agreement with the distances found in the FeS_4 tetrahedra of the minerals chalcopyrite [2.257(1) Å, 4×; HALL & STEWART, 1973] and cubanite [from 2.258(1) to 2.304(1) Å; SZYMAŃSKI, 1974]. Shorter Fe–S distances are determined in the spinel type structures of greigite (2.15 Å, 4×; Skinner et al., 1964) and daubréelite (2.21 Å, 4×; Lundqvist, 1943). The reason for this might be the inflexibility of the close-packed arrangement of the sulfur atoms. Two further minerals with FeS_4 tetrahedra are mooihoekite (Fe–S: 2.26 to 2.31 Å; Hall & Rowland, 1973); and valleriite (Fe–S: 2.30 to 2.41 Å; Evans & Allmann, 1968). In both these minerals the Fe atoms are replaced in parts by Cu atoms. In kerstite [Fe–S: 2.336(1) Å, 4×] resp. stannite [Fe–S: 2.348(2) Å, 4×] a partial replacement of the Fe atoms by Zn atoms is described (Hall et al., 1978); therefore a detailed comparison with sternbergite is problematic.

The structure of sternbergite shows, that the iron atoms are located at one crystallographic position – if the space group Ccmb is correct. Fortunately this assumption of the centric space group is supported by Mössbauer studies (Imbert & Wintenberger, 1967). These investigations show an antiferromagnetic order of the iron atoms, one valence state for all the Fe atoms, and gave evidence for the same crystallographic site for all the Fe atoms in sternbergite (cf. Vaughan & Burns, 1972). Therefore another space group than the holo-

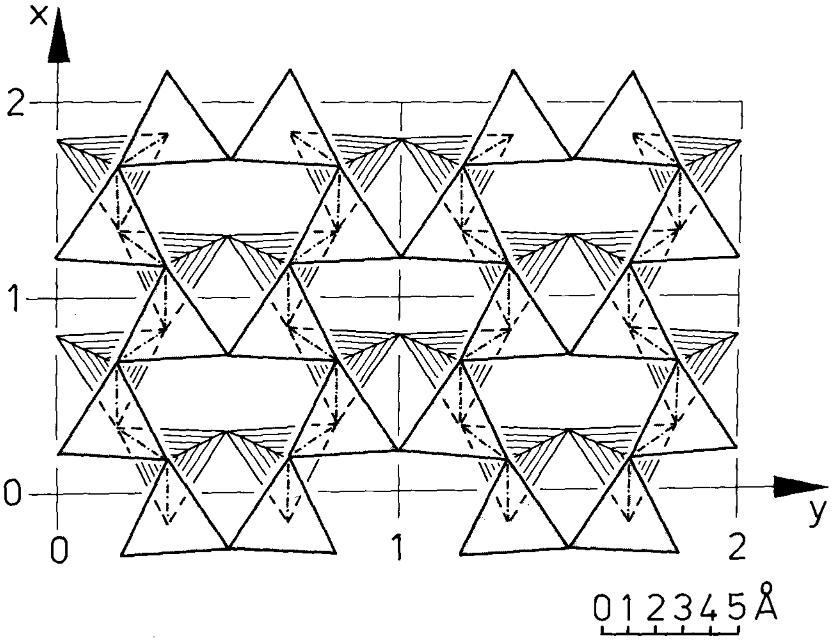

Fig. 2. Layers built up of FeS_4 tetrahedra by connection over common S atom edges and corners. Such a single layer parallel (001) from z ~0.30 to ~0.80 is given. The common edges of the FeS_4 tetrahedra are drawn as dot-dash lines.

hedral space group Ccmb – especially a hemihedral one – with a splitting of the Fe atoms to two different positions is out of discussion.

Each FeS_4 tetrahedron is combined via common S atom edges and corners to four neighbouring tetrahedra and the S atoms themselves show in parts of the structure a close packing arrangement. The connection of the FeS_4 tetrahedra results in distorted six membered rings resp. in Fe_2S_3 layers (Fig. 2) parallel to (001). In the direction c these layers are only linked by the Ag atoms, corresponding with the good cleavage perpendicular [001]. The two crystallographically different S atoms are more or less tetrahedrally coordinated by silver resp. iron atoms (cf. Table 3).

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