

## The crystal structure of freieslebenite, $\text{PbAgSbS}_3$ \*

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### Auszug

Die Struktur von Freieslebenit,  $\text{PbAgSbS}_3$ , wurde mittels dreidimensionaler Zählrohrdaten mit Hilfe der Methode der „Hauptverschiebungen“ (key shifts) bestimmt ( $R = 3,2\%$ ). Die erhaltene Struktur ist vom Modell von HELLNER (1957) verschieden; sie ist zu Marrit,  $\text{PbAgAsS}_3$ , dem As-Analogen zu Freieslebenit, isomorph. Die Daten sind: Raumgruppe  $P2_1/a$  mit  $a = 7,518(1)$ ,  $b = 12,809(4)$ ,  $c = 5,940(1)$  Å,  $\beta = 92,25(1)^\circ$  und  $Z = 4$ .

Die Struktur ist eine Überstruktur einer Substruktur vom PbS-Typ. Wohl wegen des größeren Radius von Sb gegenüber As sind die Verschiebungen der Atome aus der idealen Substruktur bei Freieslebenit kleiner als bei Marrit. Sb hat die normale trigonal-pyramidale Koordination der S-Atome mit den Abständen 2,431, 2,453 und 2,480(4) Å. Die  $\text{SbS}_3$ -Pyramiden sind voneinander isoliert. Pb weist eine deformiert-oktaedrische Koordination von sechs S-Atomen auf, mit Abständen zwischen 2,806 und 3,167(4) Å. Die  $\text{AgS}_3$ -Gruppe ist beinahe planar mit den (Ag–S)-Abständen 2,522, 2,575 und 2,687(4) Å. Ungefähr normal zur  $\text{AgS}_3$ -Ebene befindet sich ein viertes S-Atom im Abstand von 2,928(4) Å. Der Temperaturkoeffizient des Ag ist wesentlich größer und anisotroper als diejenigen der übrigen Atome, ein gemeinsamer Zug bei Strukturen dieser Art.

### Abstract

The crystal structure of freieslebenite,  $\text{PbAgSbS}_3$ , has been determined with three-dimensional counter data ( $R = 3.2\%$ ). The structure was solved by the method of key shifts. The obtained structure is different from the model proposed by HELLNER (1957); instead, it is isomorphous with marrite,  $\text{PbAgAsS}_3$ , an As analogue of freieslebenite. The crystal is monoclinic, space group  $P2_1/a$ , with  $a = 7.518(1)$ ,  $b = 12.809(4)$ ,  $c = 5.940(1)$  Å,  $\beta = 92.25(1)^\circ$  and  $Z = 4$ .

The structure is a superstructure of a PbS-type substructure. The displacements of the atoms from the ideal substructure are less in freieslebenite than in marrite, probably because of the larger atomic radius of Sb than that of As. Sb has the usual trigonal-pyramidal coordination of S atoms. The Sb–S distances

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are 2.431, 2.453 and 2.480(4) Å. The  $\text{SbS}_3$  pyramids are isolated from each other. Pb is coordinated with six S atoms in a distorted octahedral arrangement. The Pb—S distances range from 2.806 to 3.167(4) Å. Ag has three nearest S neighbours at the distances 2.522, 2.575 and 2.687(4) Å. The  $\text{AgS}_3$  group is nearly planar. A fourth S atom is at a distance of 2.928(4) Å from Ag, the Ag—S being approximately perpendicular to the  $\text{AgS}_3$  plane. The temperature factor of Ag is significantly larger and more anisotropic than those of the other atoms; this feature is common among related structures.

### Introduction

Freieslebenite,  $\text{PbAgSbS}_3$ , is one of the typical superstructures based on the PbS-type substructure. HELLNER (1957) deduced a complete structure of freieslebenite by a trial-and-error method using two-dimensional data ( $R = 31,37$  and  $41\%$  for the three projections). More recently, WUENSCH and NOWACKI (1967) determined the structure of marrite,  $\text{PbAgAsS}_3$ , an As analogue of freieslebenite. They showed that marrite is not isomorphous with the HELLNER's model of freieslebenite in spite of the same space group  $P2_1/a$  and of the close similarity of the cell dimensions (Table 1). They also observed that there were several nearly homometric structures of marrite; five different models gave the  $R$  values less than  $40\%$ .

Table 1. *Lattice constants of freieslebenite,  $\text{PbAgSbS}_3$ , marrite,  $\text{PbAgAsS}_3$ , and galena, PbS*

	Freieslebenite			Marrite	Galena*
	Present work	PALACHE <i>et al.</i> (1938)	HELLNER (1957)	WUENSCH and NOWACKI (1967)	
$a$	7.518(1)	7.53	—	7.2705(6)	8.39 Å
$b$	12.809(4)	12.79	—	12.6319(4)	12.58 Å
$c$	5.940(1)	5.88	5.95(1)	5.9853(3)	5.93 Å
$\beta$	$92.25(1)^\circ$	$92^\circ 14'$	—	$91^\circ 13.7'(2)$	$90^\circ$
$V$	571.57			549.56	$625.6 \text{ \AA}^3$

\*  $a = [110]_{\text{PbS}}$ ,  $b = \frac{2}{3} [\bar{1}10]_{\text{PbS}}$  and  $c = [001]_{\text{PbS}}$ , where  $a(\text{PbS}) = 5.93 \text{ \AA}$ .

In order to check the isomorphism of freieslebenite and marrite and also to examine more accurately the sulfur coordinations around the metal atoms, a redetermination of the structure of freieslebenite was undertaken using three-dimensional counter data. As will be described below, freieslebenite was shown to be isomorphous with marrite.

