Zeitschrift für Kristallographie, Bd. 117, S. 431–436 (1962)

The crystal structure of the anhydrous stannous sulphate

By **P. J. Rentzeperis**

Department of Mineralogy, University of Thessaloniki, Thessaloniki, Greece

With 1 figure

(Received October 8, 1962)

Auszug

Die Kristallstruktur von wasserfreiem Zinnsulfat, $SnSO_4$, wurde röntgenographisch mittels eines Norelco-Diffraktometers bestimmt. Die elementare Zelle ist rhombisch mit den Gitterkonstanten $a = 8{,}799$, $b = 5{,}319$, $c = 7{,}115$ Å, $Z = 4$, Raumgruppe D_{2h}^{16}—*Pnma*. Zinnsulfat gehört zur Baryt-Gruppe. Die unbekannten Atomkoordinaten wurden durch "trial and error" ermittelt, wobei die Isotypie mit der Baryt-Gruppe berücksichtigt wurde. Die S-Atome befinden sich im Mittelpunkt eines fast regulären Tetraeders von O-Atomen. Die Sn-Atome werden unregelmäßig von zwölf O-Atomen umgeben, welche sieben verschiedenen Tetraedern gehören.

Abstract

The crystal structure of the anhydrous stannous sulphate, $SnSO_4$, has been determined from x-ray powder data obtained with a Norelco diffractometer. The unit cell is orthorhombic with $a = 8.799$, $b = 5.319$, $c = 7.115$ Å, $Z = 4$, space group D_{2h}^{16}—*Pnma*. Stannous sulphate belongs to the barite group. The unknown parameters were determined by trial and error, after taking into account the similarity with the barite group. The S atoms lie at the center of an almost regular tetrahedron of O atoms. The Sn atoms are irregularly surrounded by twelve O atoms belonging to seven different tetrahedra.

Introduction

Anhydrous stannous sulphate, $SnSO_4$, is a highly hygroscopic white compound usually obtained in the form of a fine crystalline powder which, under the microscope, shows platy orthorhombic laths. Like all the anhydrous sulphates of bivalent metals examined so far with cations having radious smaller than unity ($r_{Sn}{}^{2+}=0.93$) the $SnSO_4$ crystals readily adsorb moisture and become opaque; however, it takes a few days until the water molecules enter the structure and cause some extra reflections of the powder. Because of the ease with which stannous salts oxidize to stannic, especially in the presence of such a strongly oxidizing agent as H_2SO_4, extreme care is necessary in preparing the salt. Perhaps difficulty of manipulation can account for the fact that no x-ray data for $SnSO_4$ have been published so far.

Experimental

Pure stannous sulphate (prepared by Dr. Theodor Schuchard and Co., Munich, Germany) was placed in an oven and kept there for two days at a constant temperature of 125 °C. From time to time the powder was taken out of the oven and ground in an agate mortar. This was necessary for two reasons: first, because the powder was dry for only a very short time, not exceeding half a minute, after which it turned to a sticky, paste-like mass, and secondly, very finely ground powder was needed for dependable intensity measurements because prefered orientation effects, especially in the $h0l$ reflections, were very strong. For example, the intensity of the 101 reflection was reduced from 412 (arbitrary units) for the unground powder (average grain dimensions about $70 \times 20 \times 10 \mu$) to only 26 for the very finely ground. The powder was further examined on a Norelco x-ray diffractometer. Owing to the rather slow entrance of water molecules in the $SnSO_4$ structure no attempt was made to render the preparation waterproof by covering it with a thin film of Scotch tape. Filtered $CuK\alpha$ radiation was employed and recordings with various settings of the diffractometer were obtained. For final indexing and intensity measurements those with very slow travel (1/8 degree per min.) were considered.

It was suspected that $SnSO_4$ might be isotypic with $PbSO_4$ and consequently with $BaSO_4$. If this were the case, then, owing to the fact that the atomic numbers of Ba (56) and Sn (50) are close to each other, the diagram of $SnSO_4$ ought to be similar to that of $BaSO_4$ in the intensities of the corresponding reflections. Although there was a general similarity, the strong 111 reflection of $BaSO_4$ was almost absent on the diagram of $SnSO_4$. Comparison with the diagrams of other anhydrous sulphates did not show any acceptable similarity to any of them. It was therefore decided to apply LIPSON's (1949) method for indexing powder diagrams of orthorhombic crystals without making any assumption. Due to the accurate $\sin^2\theta$ values of the reflections considered the indexing was effected without much difficulty. The very good agreement between observed and calculated d values for a part of the reflections considered is shown in Table 1.

The relative intensities of the reflections were obtained by measuring the area under the peaks with a planimeter. *LP* factors and f values were obtained graphically.

Lattice constants and space group

The best agreement between calculated and observed d values was obtained with the following lattice constants for the orthorhombic unit cell (Cu$K\alpha_1$, $\lambda = 1.54051$ Å):

$$a = 8.799 \pm 0.0011, \quad b = 5.319 \pm 0.0006, \quad c = 7.115 \pm 0.0009 \text{ Å},$$

$$V = 332.99 \text{ Å}^3, \quad a : b : c = 1.6542 : 1 : 1.3688.$$

For a unit-cell content of four units $SnSO_4$ a density of 4.185 $g \cdot cm^{-3}$ is deduced. No density for $SnSO_4$ is given in the literature. Although density measurements of highly hygroscopic substances are inherently difficult and the results are not always correct, a fairly good estimate was obtained from the fact that $SnSO_4$ laths, separated under the microscope and immersed in various heavy liquids, barely sank in a Clerici solution of a density 4.15 $g \cdot cm^{-3}$.

The observed reflections showed the following conditions: hkl : No condition ; $0kl$: $k+l = 2n$; $h0l$: No condition ; $hk0$: $h = 2n$, which are the conditions for the space groups D_{2h}^{16}—$Pnma$ and C_{2v}^{9}—$Pn2_1a$. The holohedral appearance of the crystals, however, and the fact that the structure is well explained by the former space group lead us to consider D_{2h}^{16}—$Pnma$ as the most probable space group for $SnSO_4$.

Determination of the structure and discussion

The lattice constants of $SnSO_4$ are close to those of barite ($a = 8.85$, $b = 5.43$, $c = 7.13$ Å, JAMES and WOOD, 1925) and one of the two possible space groups for $SnSO_4$, D_{2h}^{16}—$Pnma$, is that of barite. These, together with the fact that, notwithstanding their differences, the powder diagrams showed a general similarity, suggested that the two substances might be isotypic. Calculation of the intensities of the various reflections by employing atomic parameters found for the members of the barite group showed that, in principle, the structure of $SnSO_4$ should belong to this group, but fairly large shifts, especially of the cation, were necessary in order to bring calculated intensities into agreement with the observed. The atomic parameters listed in Table 2 gave the best agreement between observed and calculated intensities (Table 1).

Table 1. *Comparison between observed and calculated d and I values*

d_o	d_c	hkl	I_c	I_o
5.512	5.534	101	9.2	26
4.392	4.400	200	172.8	182
4.254	4.260	011	321.1	223
3.834	3.834	111	6.0	6
-	3.742	201	9.5	0
3.554	3.558	002	350.6	378
3.387	3.390	210	220.6	285
3.294	3.298	102	50.1	63
3.060	3.060	211	762.0	767
2.803	2.803	112	81.4	98
2.765	2.765	202	85.9	82
-	2.706	301	0.6	0
2.660	2.660	020	208.6	210
2.454	2.454	212	144.2	135
-	2.416	311	1.0	0
2.398	2.397	121	24.1	25
2.289	2.290	103	4.5	134
2.276	2.276	220	117.2	
2.262	2.263	302	35.8	
2.199	2.200	400	4.0	4
2.168	2.168	221	82.7	209
2.165	2.166	013	129.5	
2.130	2.130	022	92.4	86
2.101	2.103	113	64.0	367
	2.102	401	172.6	
2.087	2.088	203	7.6	
2.082	2.082	312	24.0	
2.070	2.070	122	70.8	
2.032	2.033	410	80.4	85
1.954	1.955	411	65.8	195
1.943	1.943	213	142.5	
1.917	1.917	222	94.2	82
-	1.899	321	0.6	0
1.871	1.871	402	10.7	6
1.844	1.844	303	21.2	23
1.778	1.779	004	23.5	50
1.765	1.765	412	35.6	
1.743	1.743	104	24.2	94
	1.742	313	42.3	
1.735	1.735	123	7.2	
1.721	1.724	322	1.2	35
	1.720	031	35.7	
-	1.708	501	0.7	0
1.695	1.695	420	18.1	20
	1.688	131	0.5	
1.657	1.657	114	9.9	158
1.649	1.649	204	23.3	
	1.649	421	85.7	
	1.645	230	20.8	
	1.642	223	14.4	
-	1.627	511	0.2	0
1.613	1.613	403	65.1	138
1.603	1.602	231	101.0	
1.577	1.577	502	0.4	21
1.575	1.575	214	25.5	
1.562	1.562	132	16.2	18
1.543	1.543	413	16.1	15
1.531	1.530	422	23.3	24

Table 2. *Atomic parameters in* $SnSO_4$

Atom	x	y	z
4 Sn	0.208	$\frac{1}{4}$	0.222
4 S	.069	$\frac{1}{4}$	.694
4 O_I	− .083	$\frac{1}{4}$	.597
4 O_{II}	.194	$\frac{1}{4}$	.550
8 O_{III}	.088	.020	.819

The x and z parameters of the Sn atom differ rather considerably from those found for Ba, Sr and Pb in the corresponding sulphates: 0.182 and 0.161 for Ba, 0.179 and 0.161 for Sr, 0.185 and 0.163 for Pb (WYCKOFF, 1960).

The agreement between F_c and F_o is excellent* and the R factor for the 58 non-zero and zero *hkl* reflections listed in Table 1 is 0.073.

The interatomic distances between the nearest atoms, obtained from the atomic parameters listed in Table 2, are given in Table 3.

Figure 1 shows the clinographic projection of the $SnSO_4$ structure. The SO_4 tetrahedron is almost regular with an average S—O distance 1.510 Å and O—O distances ranging from 2.447 to 2.501 Å. The Sn atom is surrounded by twelve O atoms, the two of which lie on the

---

* In the case of overlapping reflections the observed intensity for the group was distributed to the individual reflections in proportion to the corresponding calculated intensities.

Table 3. *Interatomic distances in* $SnSO_4$

Atom	Equipoint	Neighbor	Number of neighbors	Interatomic distance
		S—O distances in SO_4 tetrahedron		
S	4 *c*	O_I	1	1.505 Å
		O_{II}	1	1.503
		O_{III}	2	1.521
		O—O distances in SO_4 tetrahedron		
O_I	4 *c*	O_{II}		2.460
		O_{III}		2.501
O_{II}	4 *c*	O_{III}		2.455
O_{III}	8 *d*	O_{III}		2.447
		Sn—O distances		
Sn	4 *c*	O_I	1	2.921
		O_I	2	3.157
		O_{II}	1	2.337
		O_{II}	2	3.056
		O_{III}	2	2.400
		O_{III}	2	2.987
		O_{III}	2	3.291

same symmetry plane with the Sn atom the other ten lying symmetrically in pairs on either side of the symmetry plane. They belong to seven different tetrahedra and their distances from the Sn atom vary

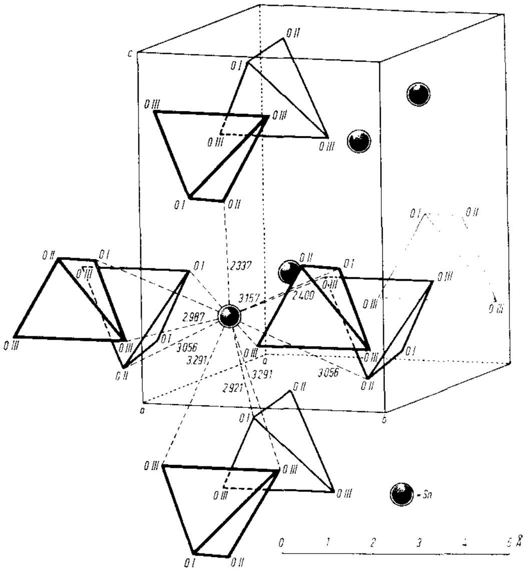

Fig. 1. Clinographic projection of the $SnSO_4$ structure, showing the spatial arrangement of the SO_4 tetrahedra and the Sn atoms

from 2.337 to 3.291 Å. Attempts to make the Sn—O distances differ less have not given good agreement between calculated and observed intensities. The O—O distances of the nearest neighbors round Sn vary from 2.447 to 3.290 Å.

Acknowledgement

Many thanks are due to the Royal Hellenic Research Foundation for supporting the research program on sulphates in our Department.

References

R. W. JAMES and W. A. WOOD (1925), The crystal structure of barytes, celestine and anglesite. Proc. Roy. Soc. [London] **109** A, 598—620.

H. LIPSON (1949), Indexing powder photographs of orthorhombic crystals. Acta Crystallogr. **2**, 43—45.

R. W. G. WYCKOFF (1960), Crystal structures. Vol. II, Chapter 8, table page 24. Interscience Publishers, Inc., NewYork.