Zeitschrift für Kristallographie, Bd. 114, S. 85—97 (1960)

The crystal structure of stibnite
A redetermination of atomic positions

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With 4 figures

(Received October 26, 1959)

Auszug

Die früher von **Hofmann** bestimmte Kristallstruktur des Antimonits (Sb_2S_3) wurde bestätigt. Die Atomkoordinaten konnten jedoch genauer bestimmt werden.

Die Struktur besteht aus parallelen bandförmigen $(Sb_4S_6)_n$-Polymeren, zusammengehalten durch zwischenmolekulare Sb-S-Bindungen (3,20, 3,33 und 3,60 Å). Die Bindungen innerhalb eines Bandes sind in ihrer Länge verschieden, weil sowohl Antimon wie Schwefel in zwei verschiedenen Koordinationsarten auftreten. Eine Hälfte der Antimonatome ist von fünf Schwefelatomen in Entfernungen von 2,49 (1), 2,68 (2) und 2,83 (2) Å umgeben, wobei jedes dieser Schwefelatome wiederum zu drei Antimonatomen gehört. Die andere Hälfte der Antimonatome und die anderen Schwefelatome (ein Drittel ihrer Gesamtanzahl) besitzen die gewöhnliche Dreiwertigkeit, beziehungsweise Zweiwertigkeit mit der Bindungslänge 2,58 Å.

Das Koordinationspolyeder des 5-koordinierten Antimons ist eine vierseitige regelmäßige Pyramide; das Antimon befindet sich ein wenig außerhalb ihrer Grundfläche.

Abstract

The crystal structure of stibnite as determined formerly by **Hofmann** has been confirmed, but a refined set of atomic coordinates has been obtained.

The structure consists of parallel ribbonlike $(Sb_4S_6)_n$ polymers linked together by the intermolecular attraction between antimony and sulphur atoms at the distances of 3.20, 3.33 and 3.60 Å. The bonds within the ribbon are different in length owing to the two different types of coordination exhibited by both antimony and sulphur. One half of the antimony atoms are surrounded with five sulphur atoms at the distances of 2.49 (1), 2.68 (2) and 2.83 (2) Å, each of these sulphur atoms being linked to three antimony atoms. The other half of the

antimony atoms and the remaining sulphur atoms — a third of the total — exhibit the usual trivalency, and bivalency, respectively, with a bond length of 2.58 Å.

The coordination polyhedron for the five-coordinated antimony is a square pyramid, the antimony atom being slightly displaced outwards of the pyramid base.

Introduction

The crystal structure of stibnite was reported as early as 1933 by HOFMANN[1]. His investigation was carried out with great care, but he used the trial-and-error method only. The present investigation was undertaken with the aim of confirming the results of HOFMANN or to correct them if necessary. In discussing HOFMANN's data on Sb_2S_3 and Bi_2S_3, WYCKOFF[2] notes that "the separation between sheets is, however, so great that a further study of these crystals should be made," and WELLS[3] speaks of the "rather unsatisfactory environment of one-half of the Sb atoms".

The crystal structures of several antimony sulfosalt minerals were recently determined, such as berthierite[4]-$FeSb_2S_4$, bournonite[5]-$CuPbSbS_3$, freieslebenite[6]-$PbAgSbS_3$, livingstonite[7]-$HgSb_4S_8$, jamesonite[8]-$FePb_4Sb_6S_{14}$ and diaphorite[9]-$Ag_3Pb_2Sb_3S_8$; the results obtained greatly contributed to better understanding of the crystallochemical relations between antimony and sulphur. These relations should appear in their clearest form without any influence of other elements in the structure of antimony sulphide.

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[1] W. HOFMANN, Die Struktur der Minerale der Antimonitgruppe. Z. Kristallogr. **86** (1933) 225—245.

[2] R. W. G. WYCKOFF, Crystal structures. Vol. 1, chap. 5, text p. 9, (Interscience Publishers, New York, 1948).

[3] A. F. WELLS, Structural inorganic chemistry, 2nd ed. (University Press, Oxford, 1950) 400.

[4] M. J. BUERGER and T. HAHN, The crystal structure of berthierite, $FeSb_2S_4$. Amer. Min. **40** (1955) 226—238.

[5] E. HELLNER und G. LEINEWEBER, Über komplex zusammengesetzte sulfidische Erze. I. Zur Struktur des Bournonits, $CuPbSbS_3$, und Seligmannits, $CuPbAsS_3$. Z. Kristallogr. **107** (1956) 150—154.

[6] E. HELLNER, Über komplex zusammengesetzte sulfidische Erze. II. Zur Struktur des Freieslebenits, $PbAgSbS_3$. Z. Kristallogr. **109** (1957) 284—295.

[7] N. NIIZEKI and M. J. BUERGER, The crystal structure of livingstonite, $HgSb_4S_8$. Z. Kristallogr. **109** (1957) 129—157.

[8] N. NIIZEKI and M. J. BUERGER, The crystal structure of jamesonite, $FePb_4Sb_6S_{14}$. Z. Kristallogr. **109** (1957) 161—183.

[9] E. HELLNER, Über komplex zusammengesetzte Spießglanze. III. Zur Struktur des Diaphorits, $Ag_3Pb_2Sb_3S_8$. Z. Kristallogr. **110** (1958) 169—174.

Origin and preparation of the specimens

The present investigation was carried out both on natural and synthetic crystals of Sb_2S_3. The provenance of stibnite minerals is from Zajača mine, Yugoslavia. In order to obtain synthetic crystals a slow sublimation of Sb_2S_3 (p. a.) at 600 °C was carried out in a supremax glass tube sealed under the vacuum of 0,1 mm Hg. In these conditions needle-shaped crystals up to 2 cm long were grown. Elongated in the *c*-axis direction, they possessed well developed planes in the vertical zone (this was not the case with the mineral). The purity of the starting material, the definitive geometry of synthetic crystals, and their appropriate small size, contributed to an easier and more precise determination of crystallographic parameters.

Unit cell and space group

Oscillation photographs about three crystallographic axes as well as those about [110] direction — combined with b/a ratio from the best values of the φ angular coordinates given by DANA[10] — were used in the measurement of lattice dimensions. Results of the present study, based on $\mathrm{Cu}K\alpha = 1.542$ Å, are compared with those of HOFMANN in Table 1.

Table 1. *Cell dimensions for* Sb_2S_3 (in Å)

	a	*b*	*c*
HOFMANN	11.20	11.28	3.83
Present study	11.25 ± 0.02	11.33 ± 0.02	3.84 ± 0.01

The observed density[10] is 4.63 ± 0.02 g cm^{-3}, and that calculated for four formula units of Sb_2S_3 on the basis of new cell dimensions, is 4.61 g cm^{-3}.

The systematically absent reflexions were only $h0l$ for $h + l$ odd, and $0kl$ for k odd. In the orthorhombic system, these extinctions are consistent with space groups $Pbnm - D_{2h}^{16}$ and $Pbn2_1 - C_{2v}^{9}$. However, the morphology, the lack of pyroelectric effect and the etching figures of stibnite indicate the centrosymmetrical space group *Pbnm* as probable, which is in agreement with HOFMANN's asignement. The same is supported by the almost exact correspondence between the intensities of the $hk0$ and $hk2$ pairs of reflexions.

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[10] J. D. DANA and E. S. DANA, The system of mineralogy. Vol. 1 (J. Wiley and Sons, New York, 1941) 270.

In space group *Pbnm*, with (001) mirror planes (at $\frac{1}{4}c$ and $\frac{3}{4}c$) separated 1.92 Å as in stibnite, both packing consideration of antimony and sulphur atoms (with van der Waals radii[11] of 2.2 Å and 1.85 Å respectively) as well as the constancy of $I(hk0)/I(hk2)$ ratio exclude all positions except $4c$. With $Z = 4\,Sb_2S_3$ it is, therefore, necessary to find out five such sets of atomic positions.

Structure determination

With the use of an integrating Weissenberg goniometer, normal-beam photographs of the *hk*0 reflections and equi-inclination photographs of the *hk*1 and *hk*2 reflections were made both from synthetic and natural specimens; a four-film technique was applied. The relative intensities of the reflections were deduced from the microphotometric measurements of optical densities of spots; for very weak reflexions only visual estimations were made.

Stibnite is a highly absorbing material ($\mu = 1.060\ \mathrm{cm}^{-1}$ for Cu$K\alpha$ radiation) so an absorption correction was indispensable and it was carried out with the use of the absorption factors for cylindrical specimens[12]. A natural crystal was ground to the shape of a cylinder with a diameter of 0.16 mm ($\mu R = 8.5$) in the (001) cross section. The mean diameter of the synthetic needle investigated was 0.02 mm ($\mu R = 1.06$). Corrections for polarization and Lorentz factors were made in the usual way. The scale factor was determined by means of the Wilson statistics[13].

In order to obtain data completely independent of those of Hofmann, the Patterson projection $P(xy)$ was calculated with the *hk*0 intensities of synthetic crystal; it is given in Fig. 1. The preliminary antimony coordinates, as deduced from this projection, are:

$$x_{\mathrm{I}} = 0.325 \qquad x_{\mathrm{II}} = 0.037$$
$$y_{\mathrm{I}} = 0.029 \qquad y_{\mathrm{II}} = 0.147.$$

By the use of the above values of antimony parameters the signs of the $F(hk0)$ structure amplitudes were evaluated, neglecting — at this stage — the contribution of the sulphur atoms. Separate calcula-

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[11] L. Pauling, The nature of the chemical bond. (Cornell University Press, Ithaka, 1940) 189.

[12] A. J. Bradley, The absorption factor for the powder and rotating-crystal methods of x-ray crystal analysis. Proc. Physic. Soc. [London] **47** (1935) 879–899.

[13] A. J. C. Wilson, Determination of absolute from relative x-ray intensity data. Nature [London] **150** (1942) 152.

tions were further performed with the intensities from natural and synthetic specimens. This was done in order to estimate the influence of the marked asterism of the spots (due to mechanical deformation of

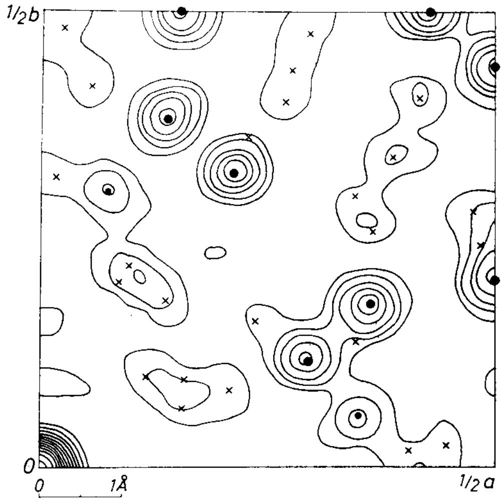

Fig. 1. Patterson projection along [001], on which antimony—antimony and antimony—sulphur peaks (fromfinal atomic coordinates) are inserted. Doubly weighted and singly weighted Sb—Sb peaks are indicated by large and small dots respectively and doubly weighted Sb—S peaks are indicated by crosses.

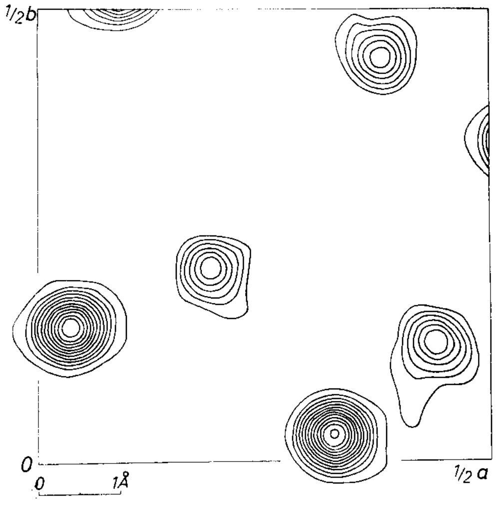

Fig. 2. Electron-density projection along [001]. Contours are drawn at intervals of $5e\text{Å}^{-2}$ and $10e\text{Å}^{-2}$ for sulphur and antimony peaks respectively, zero-electron line for sulphur peaks being omitted.

the mineral) on the intensity measurements or, eventually, on the values of the final atomic coordinates.

In the first Fourier projection on the (001) plane the peaks of the sulphur atoms appeared neatly resolved in addition to those of the antimony atoms. With the redetermined signs, taking into account x and y parameters of all atoms, a second Fourier synthesis was computed (Fig. 2). Only few very low spurious peaks appeared on the electron-density projection; in the map they are omitted. The heights of the nearly spherical peaks of the three crystallographically independent sulphur atoms were practically equal — the same was true for the antimony peaks — and the ratio of sulphur and antimony maximum heights was in accordance with the ratio of their atomic numbers.

Table 2. *Atomic coordinates in stibnite*

		Hofmann	Present investigation		σ
			Synthetic	Natural	
Sb_{I}	x	0.328	0.326	0.326	0.0037
	y	0.031	0.030	0.030	0.0034
	z	$^1/_4$	$^1/_4$	$^1/_4$	
Sb_{II}	x	0.039	0.036	0.036	0.0042
	y	0.149	0.149	0.149	0.0041
	z	$^3/_4$	$^3/_4$	$^3/_4$	
S_{I}	x	0.883	0.880	0.879	0.0148
	y	0.047	0.055	0.054	0.0145
	z	$^1/_4$	$^1/_4$	$^1/_4$	
S_{II}	x	0.439	0.441	0.440	0.0142
	y	0.125	0.131	0.130	0.0142
	z	$^3/_4$	$^3/_4$	$^3/_4$	
S_{III}	x	0.194	0.189	0.190	0.0129
	y	0.208	0.214	0.213	0.0144
	z	$^1/_4$	$^1/_4$	$^1/_4$	

From the refined [001] electron-density projections the final x and y coordinates of all atoms (for synthetic and natural crystals) were evaluated using the Booth method[14]. The results of the present investigation and, for comparison, also those of Hofmann, are given in Table 2.

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[14] A. D. Booth, Fourier technique in x-ray organic structure analysis. (University Press, Cambridge, 1948) 62.

To find out the third coordinate for each structurally independent atom, which can be $\frac{1}{4}c$ or $\frac{3}{4}c$, the trial-and-error procedure was applied. The calculation of structure amplitudes for some forty *hkl* (with $l = 2n \pm 1$) reflections was performed, arbitrarily assuming $z = {}^1/_4$ for $\mathrm{Sb_I}$. Good agreement between F_c and F_0 was obtained only with the z parameters of Table 2.

By comparing the values of the second and third column of Table 2, it is seen that the structural imperfections and small plastic deformations of natural crystals had an insignificant influence on the determination of atomic parameters.

To assess the differences between the values of atomic coordinates of the present investigation and those of HOFMANN the standard deviation was calculated using the formula[15]:

$$\sigma\,(x) = \frac{2\pi\,[\Sigma h^2\,(\Delta F)^2]^{1/2}}{A \cdot a\,(\delta^2\,\varrho/\delta\,x^2)}\,.$$

The curvature of peak electron density, $\delta^2\varrho/\delta x^2$, was obtained from the (001) Fourier projection of the natural crystal by a graphical method, assuming

$$\varrho\,(x) = \varrho_0 \exp - (px^2).$$

Standard deviations of atomic coordinates calculated in such a way are reported in the last column of Table 2. According to the theory of errors, if the distribution of errors is Gaussian, the probable error (with $50\,^0/_0$ probability) of an observation is $\pm\,0.6745\,\sigma$; it has $99.7\,^0/_0$ probability of being within a $\pm 3\sigma$ interval.

It follows, therefore, that all the differences between the present and HOFMANN's atomic coordinates greater than 0.012 Å for antimony and 0.042 Å for sulphur (i. e. 0.0012 or 0.0037 in fractions of $a \sim b$ parameters) are statistically significant. Here the values of 0.004 Å and 0.014 Å were used as the average standard deviation of antimony and sulphur parameters respectively.

The comparison between F_0 for natural specimen and F_c (Table 3) indicates a good agreement. For evaluating F_c the corresponding atomic scattering factors from Internationale Tabellen[16] were used by

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[15] D. W. J. CRUICKSHANK, The accuracy of electron-density maps in x-ray analysis with special reference to dibenzyl. Acta Crystallogr. 2 (1949) 65—82.

[16] Internationale Tabellen zur Bestimmung von Kristallstrukturen. Vol. 2. (Borntraeger, Berlin, 1935) 571.

Table 3. *Observed and calculated structure factors*

h k l	F_o	$\frac{1}{2}F_c$	h k l	F_o	$\frac{1}{2}F_c$	h k l	F_o	$\frac{1}{2}F_c$	h k l	F_o	$\frac{1}{2}F_c$
2 0 0	27	23	1 3 0	95	-92	3 6 0	62	63	8 9 0	6	-6
4 0 0	0	3	2 3 0	68	65	4 6 0	24	26	9 9 0	0	-1
6 0 0	63	73	3 3 0	23	20	5 6 0	74	76	10 9 0	46	-49
8 0 0	61	-67	4 3 0	56	-56	6 6 0	31	26	11 9 0	21	21
10 0 0	23	-27	5 3 0	93	-87	7 6 0	30	-26			
12 0 0	10	-13	6 3 0	4	-7	8 6 0	29	-28	1 10 0	48	-49
14 0 0	35	-51	7 3 0	8	-9	9 6 0	50	43	2 10 0	43	-42
			8 3 0	0	-1	10 6 0	20	-22	3 10 0	0	-4
0 2 0	59	58	9 3 0	52	52	11 6 0	18	21	4 10 0	11	-10
0 4 0	18	-12	10 3 0	31	-31	12 6 0	0	-7	5 10 0	19	19
0 6 0	85	73	11 3 0	15	-8	13 6 0	23	-30	6 10 0	11	-10
0 8 0	22	19	12 3 0	6	8				7 10 0	42	-39
0 10 0	61	-61	13 3 0	27	30	1 7 0	30	22	8 10 0	0	4
0 12 0	39	-34	14 3 0	9	-6	2 7 0	42	42	9 10 0	15	15
0 14 0	6	10				3 7 0	74	70	10 10 0	16	21
			1 4 0	0	-6	4 7 0	70	-64			
1 1 0	16	18	2 4 0	108	-107	5 7 0	9	8	1 11 0	19	-14
2 1 0	14	-14	3 4 0	41	43	6 7 0	21	-14	2 11 0	38	31
3 1 0	87	82	4 4 0	60	-54	7 7 0	6	5	3 11 0	25	-21
4 1 0	26	-27	5 4 0	53	52	8 7 0	15	12	4 11 0	8	3
5 1 0	33	-34	6 4 0	49	46	9 7 0	0	-3	5 11 0	0	1
6 1,0	52	-56	7 4 0	4	-6	10 7 0	23	-25	6 11 0	33	33
7 1 0	0	4	8 4 0	9	-10	11 7 0	27	-27	7 11 0	9	-4
8 1 0	28	-33	9 4 0	29	29	12 7 0	15	15	8 11 0	37	38
9 1 0	46	43	10 4 0	29	31				9 11 0	13	-12
10 1 0	27	-28	11 4 0	33	33	1 8 0	46	-44			
11 1 0	43	-47	12 4 0	33	41	2 8 0	30	22	1 12 0	21	-17
12 1 0	17	-20	13 4 0	18	-19	3 8 0	27	-27	2 12 0	20	21
13 1 0	21	-24				4 8 0	23	21	3 12 0	19	20
14 1 0	0	4	1 5 0	0	-7	5 8 0	14	-15	4 12 0	15	15
			2 5 0	84	80	6 8 0	0	-1	5 12 0	50	49
1 2 0	62	-59	3 5 0	31	29	7 8 0	73	-71	6 12 0	16	-15
2 2 0	55	-55	4 5 0	5	-4	8 8 0	15	-19	7 12 0	7	12
3 2 0	56	-51	5 5 0	18	-12	9 8 0	17	-19	8 12 0	14	18
4 2 0	60	-54	6 5 0	43	38	10 8 0	18	-17			
5 2 0	64	-64	7 5 0	26	-19	11 8 0	7	6	1 13 0	38	38
6 2 0	46	42	8 5 0	64	63	12 8 0	0	-2	2 13 0	15	14
7 2 0	90	-95	9 5 0	13	15				3 13 0	6	1
8 2 0	9	-10	10 5 0	12	14	1 9 0	41	-33	4 13 0	23	-23
9 2 0	16	-19	11 5 0	14	-14	2 9 0	40	29	5 13 0	21	25
10 2 0	0	1	12 5 0	27	29	3 9 0	28	-27	6 13 0	17	20
11 2 0	0	-2	13 5 0	4	-3	4 9 0	71	-69			
12 2 0	27	30				5 9 0	16	13	1 14 0	12	-16
13 2 0	9	-11	1 6 0	44	-43	6 9 0	13	-14	2 14 0	25	29
14 2 0	11	-13	2 6 0	31	32	7 9 0	4	-4	3 14 0	9	-6

applying an average temperature factor, $\exp\left[-B\left(\frac{\sin\theta}{\lambda}\right)^2\right]$, with $B = 1.47$ Å². This value of B was derived from the slope of the most probable line through the points obtained by plotting $\ln F_o/F_c$ against $\left(\frac{\sin\theta}{\lambda}\right)^2$.

Taking into account all 167 *hk*0 reflections, the discrepancy factor $R = \Sigma\left||F_o| - |F_c|\right|/\Sigma\,|F_c|$ is 0.11. The influence of the secondary extinction was not appreciable. The equality of the x and y parameters from two separate measurements (on natural and synthetic crystals) as well as the low mean divergence of F_o and F_c offered a satisfactory justification for not making any further refinement.

Description and discussion of the structure

The interatomic distances and the bond angles, obtained from the final atomic coordinates (third column of Table 2), are given in Table 4 along with the values of HOFMANN. Some of these interatomic distances (which define the type of the structure) are also shown in the projection of the structure on the (001) plane, Fig. 3.

Table 4. *Interatomic distances* (Å) *and bond angles*

(*a*) Within a ribbon			(*b*) Between ribbons		
	Present investigation	HOFMANN		Present investigation	HOFMANN
Sb_I—S_{II}	2.57 (2)	2.50	Sb_I—S_{II}	3.20 (1)	3.14
Sb_I—S_{III}	2.58 (1)	2.51	Sb_I—S_{III}	3.60 (1)	3.65
Sb_I—S_I	3.15 (2)	3.18	Sb_{II}—S_{II}	3.33 (2)	3.38
Sb_{II}—S_I	2.49 (1)	2.38	S_I—S_{II}	3.63	
Sb_{II}—S_{III}	2.68 (2)	2.67	S_{II}—S_{III}	3.33	
Sb_{II}—S_I	2.82 (2)	2.83			
S_I—S_I	3.55				
S_I—S_{III}	3.67				
S_{II}—S_{III}	3.57				
Sb_{II}—Sb_{II}	3.97				
Sb_I—Sb_{II}	4.02				

Sb_I—Sb'_I = Sb_{II}—Sb'_{II} = S_I—S'_I = S_{II}—S'_{II} = S_{III}— S'_{III} = z = 3,84 Å.
All the other interatomic distances are greater than the sum of van der Waals radii.

S_{II}—Sb_I—S_{III} = 87.72°
S_{II}—Sb_I—S'_{II} = 96.57
S_I—Sb_{II}—S_{III} = 90.17
S_{III}—Sb_{II}—S'_{III} = 91.50
S_I—Sb_{II}—S_I = 83.55
S_I—Sb_{II}—S'_I = 85.70

S_{III}—Sb_{II}—S_I = 93.83°
Sb_I—S_{II}—Sb'_I = 96.57
Sb_I—S_{III}—Sb_{II} = 99.37
Sb_{II}—S_{III}—Sb'_{II} = 91.50
Sb_{II}—S_I—Sb_{II} = 96.45
Sb_{II}—S_I—Sb'_{II} = 85.70

Considering first only the strong bonds (Sb—S separations from 2.49 to 2.82 Å), it is seen that one-half of the contents of the unit cell (4 Sb and 6 S) are grouped together. The arrangement of the atoms in the group is such to allow for a [001] two-fold screw axis at its center. The symmetry operation of this screw axis results in the formation of an infinite $(Sb_4S_6)_n$ ribbon, which is parallel to the c axis, i. e. the needle axis. Schematic representation of a part (through four unit cells) of this ribbon, projected on (010) plane, is shown in Fig. 4*a*. The distribution of the Sb—S bonds in such an infinite complex is the following.

Each Sb_I atom is bonded to three sulphur atoms ($2\,S_{II}$ at 2.57 Å and $1\,S_I$ at 2.58 Å), these Sb_I—S bonds being the lateral edges of a trigonal pyramid with Sb at the vertex and S atoms at the corners of the basal plane. This polyhedron is slightly distorted because of the differences in the dimensions of the base edges and bond angles: two base edges (S_{II}—S_{III}) amount to 3.57 Å and the third to 3.84 Å $= z$. The corresponding bond angles are (S_{II}—Sb_I—S_{III}) $=$ 87,72° and (S_{II}—Sb_I—S'_{II}) $=$ 96.57°.

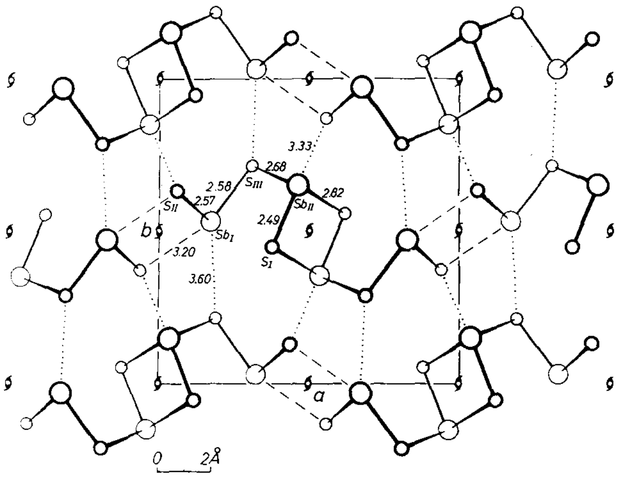

Fig. 3. Arrangement of atoms in the c-axis projection and interatomic distances

Five sulphur atoms belong to each Sb_{II} atom. They are disposed at the corners of slightly distorted square pyramid, whose lateral edges in pairs amount to (S_I—S_{III}) 3.67 Å and (S_I—S_I) 3.55 Å, and whose base edges are: (S_{III}—S'_{III} $=$ S_I—S'_I $= z =$) 3.84 Å and (S_{III}—S_I $=$ S'_{III}—S'_I $=$) 4.02 Å.

The lengths of Sb_{II}—S bonds, one of 2.49 Å (to S_I at the vertex of pyramid), two of 2.68 Å and two of 2.82 Å (to S_{III} and S_I atoms respectively at the base corners), are not so uniform as the Sb_I—S bond lengths. It follows from these bond lengths and the corresponding bond angles (Table 4) that the Sb_{II} atom is slightly (0.12 Å) shifted outside of the volume of pyramid and towards the S_{III} atoms, as is shown on Fig. 3.

The polyhedra described are connected to the infinite ribbon through the common sulphur atoms: each S_I atom is bonded to one Sb_{II} atom, which lies in the same (001) symmetry plane, and to two translation-equivalent Sb_{II} atoms from the next opposite symmetry planes; each S_{II} belongs to two translation-equivalent Sb_{I} atoms lying on the next opposite symmetry planes; each S_{III} atom is bonded to one Sb_{I} atom from the same, and to two Sb_{II} atoms from the opposite, symmetry planes. The basal planes of both trigonal and square pyramid are parallel to the long axis of the ribbon.

According to the empirical formula of PAULING[17] the amount of ionic character is $1 - \exp\{-c(X_A - X_B)^2\}$, (where $X_A - X_B$ is the difference in electronegativity of bonded atoms, and $c = {}^1/_4$), the

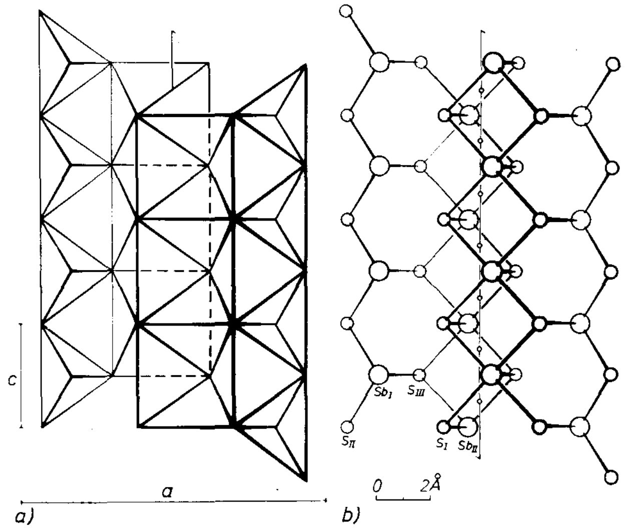

Fig. 4. Projection of a ribbon on (010) plane. *a* The joining of the coordination polyhedra: trigonal $\text{Sb}_{\text{I}}\text{S}_3$ pyramids and square S_5 pyramids (around Sb_{II}). *b* Chemical bonding of atoms.

partial ionic character of the Sb—S bond amounts to $12\,^0/_0$, and so the bond can be treated as approximately covalent. The values of 2.49 Å, 2.57 Å and 2.58 Å for the Sb—S bond lengths approach the sum of covalent radii $R_{\text{Sb}} + R_{\text{S}} = 2.48$ Å, [taking $R_{\text{Sb}} = 1.44$ Å $= \frac{1}{2}$ (Sb—Sb) in antimony, and $R_{\text{S}} = 1.04$ Å $= \frac{1}{2}$ (S—S) in the S_8 molecule of rhombic sulphur]; the values of 2.68 Å and 2.82 Å exceed this sum.

The ribbon-like $(\text{Sb}_4\text{S}_6)_n$ polymers, related by the [001] two-fold screw axes at $(0,\frac{1}{2},0)$ or $(\frac{1}{2},0,0)$, can be regarded as forming a zig-zag sheet, which is roughly perpendicular to the *b* axis. Here the shortest

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[17] L. PAULING[11], 69.

Sb_I—S_{II} distance is 3.20 Å, so that a much weaker type of chemical bonding fastens the bands into a sheet. These vertical sheets, in turn, are held together into a crystal body two sets of weak residual Sb—S interactions at the distances of 3.33 Å and 3.60 Å, the sum of van der Waals radii for Sb and S being 4.05 Å.

Two features of the crystal structure of stibnite just described are of particular crystallochemical interest. Dealing with such a simple compound like stibnite, one would expect — this was also our working hypothesis — a more ideal structure with regard to the interatomic distances and the coordination polyhedra. It is found, however, that:

(1) Besides the equality of Sb_I—S distances, there are three values for the Sb_{II}—S bond length; this is probably conditioned by the mutual interaction of the directional tendency of the bonds and the packing requirements. The same dissipation of Sb—S distances was recently observed in several antimony sulfosalt minerals as in berthierite[4], livingstonite[7] and jamesonite[8].

(2) Symmetrically unrelated antimony atoms of the stibnite structure also differ in their number of bonded sulphur atoms. Two described coordination types of sulphur displayed by Sb_I and Sb_{II} atoms also exist in the two types of Sb atoms in berthierite; moreover, there are completely analogous coordinations in the crystal structures of livingstonite, jamesonite and also in freieslebenite[6].

The spatial configuration of the electronic cloud of the antimony atom gives a satisfactory explanation of its described stereochemical behaviour. Trivalent antimony atom can complete its $5s^2p^3$ valency shell to an octet of four tetrahedrally arranged pairs of electrons, forming three covalent bonds with trigonal pyramidal arrangement. This is the case with (Sb_IS_3) groups, where three *p* orbitals are engaged in bond formation.

When, in addition to three *p* orbitals, two d_γ atomic orbitals (i.e. those with their maxima in the direction of *p* orbitals) of the antimony valency shell are also used for bond formation, the most probable arrangement of six pairs of electrons is at the corners of an octahedron[18], the hybridization being sp^3d^2; a 5-coordinated complex of square pyramidal shape is formed. The lone pair of electrons on the remaining corner of the octahedron exercises a stronger electrostatic repulsion on bond pairs than those between them[19], and so the central antimony

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[18] J. W. Linnet and C. E. Mellish, Directed valency in certain molecules and complex ions. Trans. Faraday Soc. **50** (1954) 665—670.

atom in the $(Sb_{II}S_5)$ complex is slightly displaced out of the square pyramid. This departure of the central Sb_{II} atom from coplanarity with the four S ligands at the corners of basal plane cannot be neglected; it is also seen on the (010) projection of livingstonite structure[7]. ALDERMAN and OWSTON's criticism[20] of the structure of K_2SbF_5, determined by BYSTRÖM and WILHELMI[21], where the antimony atom lies slightly below the basal plane of the square pyramid, was not justified.

With the present investigation of the crystal structure of stibnite the general lines of HOFMANN's structure were confirmed. This was indirectly also done[22] by the x-ray study of isostructural Sb_2Se_3. However, the differences between ours and HOFMANN's data on Sb—S separations (except for 2.68 and 2.82 Å) are significant; they exceed 0.0146 Å, the value of the mean standard deviation for the Sb—S bond length, more than by a factor of 3.

The physical properties of stibnite such as (1) cleavages, (010) perfect and easy, (100) and (110) imperfect, (2) translation gliding parallel to (010) in the [001] direction, (3) easy bending about [100] can be explained as the result of the structural nature described above.

I am very much indebted to Prof. D. GRDENIĆ (Laboratory for general and inorganic chemistry, Faculty of science, University Zagreb) for many valuable suggestions during the whole work.

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[19] J. A. POPLE, The molecular orbital theory of chemical valency. V. The structure of water and similar molecules. Proc. Roy. Soc. [London] A **202** (1950) 323—336.

[20] P. R. H. ALDERMAN and P. G. OWSTON, The square pyramidal configuration in a five-co-ordinate nitrosyl complex. Nature [London] **178** (1956) 1071—1072.

[21] A. BYSTRÖM and K.-A. WILHELMI, The crystal structure of K_2SbF_5 and isomorphous compounds. Arkiv Kemi **3** (1952) 461—467.

[22] N. W. TIDESWELL, F. H. KRUSE and J. D. MCCULLOUGH, The crystal structure of antimony selenide, Sb_2Se_3. Acta Crystallogr. **10** (1957) 99—102.