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The Crystal Structure of Antimony Selenide, Sb_2Se_3

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The isomorphism of Sb_2Se_3 with Sb_2S_3 has been confirmed through a re-determination and refinement of the structure of Sb_2Se_3. Antimony selenide is orthorhombic, *Pbnm*, with $a = 11{\cdot}62 \pm 0{\cdot}01$, $b = 11{\cdot}77 \pm 0{\cdot}01$, $c = 3{\cdot}962 \pm 0{\cdot}007$ Å and $z = 4$. The 'bonded' Sb–Se distances range from 2·576 Å to 2·777 Å, while the 'non-bonded' Sb–Se separations start at 2·98 Å. The Se–Sb–Se angles range from 86·6° to 96·0° and the Sb–Se–Sb angles from 91·0° to 98·9°. The structure consists of chains parallel to the *c* or needle axis. The strongest bonds (shortest separations) are within the chains; however, there are strong interactions between the chains. All important features of the structure reported by Hofmann for Sb_2S_3 (stibnite) have been confirmed.

Introduction

Antimony selenide, Sb_2Se_3, has been shown by Dönges (1950) to be isostructural with antimony sulfide (Hofmann, 1933). In his investigation, Dönges assumed the same atomic parameters reported by Hofmann for Sb_2S_3 and found reasonably good agreement between calculated and observed intensities for the twenty-one reflections of the type ($h00$), ($hh0$), and ($0k0$) which he considered. Although this treatment left little doubt regarding isomorphism between the sulfide and selenide, it did not permit calculation of accurate bond distances and bond angles in the selenide.

The main objective of the present study of Sb_2Se_3 has been the determination of accurate atomic parameters, distances, and angles in this substance. However, an important secondary objective has been the confirmation of certain features of the Sb_2S_3 structure. Although Hofmann's investigation was carried out with great care, it was done without the use of Fourier series or modern refinement procedures. Certain features of the reported structure have been questioned by Wyckoff (1948), and Wells (1950) speaks of the 'rather unsatisfactory environment of one-half of the Sb atoms'. Since only small shifts in the x and y parameters of the sulfur atoms would be needed to equalize the Sb–S distances in stibnite, a detailed examination and refinement of the structure of Sb_2Se_3 was considered worthwhile.

Experimental

Crystalline antimony selenide was prepared from antimony and selenium of high purity obtained from Messrs Johnson Matthey and Co. Carefully weighed stoichiometric amounts of the powdered elements were mixed and placed in a quartz tube, which was then evacuated and sealed off. The tube was placed in a furnace and heated to 900° C. for two hours, after which it was slowly cooled to room temperature. The material was highly crystalline, and individual crystals suitable for X-ray analysis were found in cavities in the product. These were needles along the c axis, as is the habit with stibnite. A number of the smaller crystals 1–2 mm. long and having approximately circular cross-sections about 0·1 mm. in diameter were selected and mounted.

Zero- and upper-level Weissenberg photographs, using four films, were prepared about the needle axis with Cu $K\alpha$ radiation. In spite of its lower absorption, molybdenum radiation was not used because of the strong fluorescence of selenium at this wavelength. For purposes of lattice-constant and space-group determinations, rotation and Weissenberg photographs about the a axis were also prepared. Unfiltered powder photographs of pure KCl were superimposed on some of the films for calibration purposes. Unit-cell dimensions for Sb_2Se_3 found in the present investigation, based on Cu $K\alpha = 1{\cdot}542$ Å, are given in Table 1, together with those reported by Dönges for Sb_2Se_3 and by Hofmann for Sb_2S_3. The observed density, Dm, of 5·8 g.cm.$^{-3}$ requires 4 Sb_2Se_3 per unit cell. The density calculated from the X-ray data in the present study, D_x, is 5·886 g.cm.$^{-3}$.

Table 1. *Cell dimensions in* Sb_2Se_3 *and* Sb_2S_3

	Sb_2Se_3, present study	Sb_2Se_3, Dönges	Sb_2S_3, Hofmann
a (Å)	11·62 ±0·01	11·58	11·20
b (Å)	11·77 ±0·01	11·68	11·28
c (Å)	3·962±0·007	3·98	3·83

The indexed photographs showed no systematic absences for hkl or for $hk0$. Absences were noted in $h0l$ for $h+l$ odd and in $0kl$ for k odd. These observations are in agreement with Hofmann's space group assignment of *Pbnm* (or $Pbn2_1$) for Sb_2S_3. The almost exact correspondence between intensities for $hk0$ and $hk2$ is in keeping with the layer structure based on *Pbnm* which was proposed by Hofmann. This observation, together with the non-observance of a pyroelectric effect in stibnite, indicates that the noncentrosymmetric space group is improbable. The space group *Pbnm* is thus, at least tentatively, taken as the correct one. With mirror planes separated by $\frac{1}{2}c$ or 1·981 Å, and with atoms having van der Waals radii of approximately 2 Å, packing considerations eliminate all positions in *Pbnm* except 4(*c*). We thus have 2 Sb and 3 Se to place in five such sets of positions.

A set of $|F_o|$ values for the 173 independent observed *hk*0 reflections was obtained from the visually estimated intensities by use of the usual Lorentz and polarization factors and through use of absorption factors based on the assumption of a cylindrical specimen. The crystal habit, which includes numerous prism faces of the type *hk*0, makes the latter assumption reasonably valid. Measurement of the crystal used for the intensity data showed a nearly uniform diameter of 0·10 mm. Although this is often considered small enough for crystals used in X-ray diffraction studies, the high absorption for Cu $K\alpha$ radiation ($\mu = 1088$, $\mu R = 5{\cdot}5$) made correction necessary in this case.

It was assumed that the atomic parameters reported for Sb_2S_3 would represent a satisfactory trial structure for Sb_2Se_3, and the signs of the F_o values were fixed initially on this basis. A Fourier synthesis on (001) showed five nearly circular peaks of the right relative heights to correspond to 2 Sb and 3 Se atoms. No other significant peaks appeared. By use of the coordinates of these peak maxima, a new set of F_c values was calculated which involved sign changes for only a few terms. A second Fourier synthesis was then prepared (Fig. 1) and the corresponding F_c values were calculated. These showed no further changes in sign. The atomic parameters from the second Fourier synthesis were corrected for series-termination errors through use of an F_c synthesis in the usual way. The resulting parameters and backshift corrections are given in Table 2.

At this stage, the value of $R = \Sigma||F_o|-|F_c||\div\Sigma|F_o|$ was 0·23 when an isotropic temperature factor $B = 1{\cdot}10$ Å^2 was used. Although this indicated that the structure was probably close to being correct, it was decided that a least-squares refinement on SWAC by the method of Sparks, Prosen, Kruse & Trueblood (1956) would be worthwhile. In this procedure, anisotropic temperature factors (three for each atom) were used. The temperature factor applied to each atom thus takes the form:

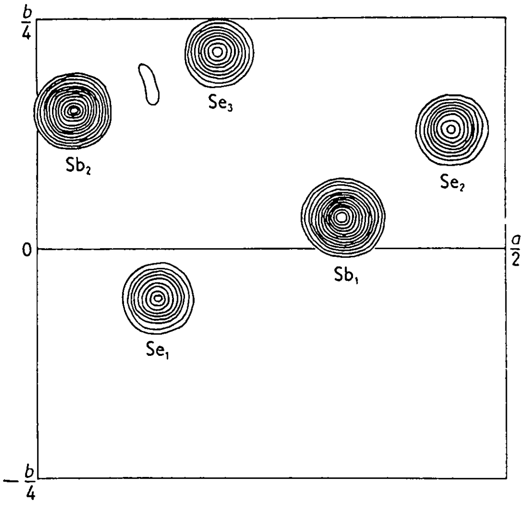


Fig. 1. Fourier projection on (001). Contour interval 10 e.Å^{-2}. Zero contour not shown.

$$\exp\left[-(B_{xx}h^2+B_{xy}hk+B_{yy}k^2)\right] .$$

Five least-squares cycles resulted in levelling off the value of R at 0·15. The final atomic parameters from the least-squares refinement are given in Table 2 along with those from the Fourier refinement in the present study and the parameters reported by Hofmann for Sb_2S_3. The standard deviations of the final parameters, computed from the least-squares determinant coefficients, are given in the last column of the table. The anisotropic temperature factors resulting from the least-squares refinement, with their standard deviations, are given in Table 3. The calculated and observed structure factors are compared in Table 4.

Table 2. *Atomic parameters in antimony sulfide and antimony selenide*

			Present investigation (Sb_2Se_3)			
		Hofmann (Sb_2S_3) Dönges (Sb_2Se_3)	Fourier refinement	Backshift corrections	Least-squares refinement	Standard deviation (σ)
Sb_I	x	0·328	0·326	−0·001	0·3280	0·00049
	y	0·031	0·031	0·000	0·0305	0·00044
Sb_{II}	x	0·039	0·040	0·000	0·0397	0·00059
	y	0·149	0·146	−0·001	0·1478	0·00043
Se_I	x	0·883	0·872	0·000	0·8732	0·00071
	y	0·047	0·054	0·000	0·0534	0·00062
Se_{II}	x	0·439	0·441	−0·001	0·4434	0·00081
	y	0·125	0·132	0·000	0·1302	0·00074
Se_{III}	x	0·194	0·195	0·001	0·1935	0·00073
	y	0·208	0·212	−0·002	0·2132	0·00069

Table 3. *Anisotropic temperature factors*

(Values are in Å^2)

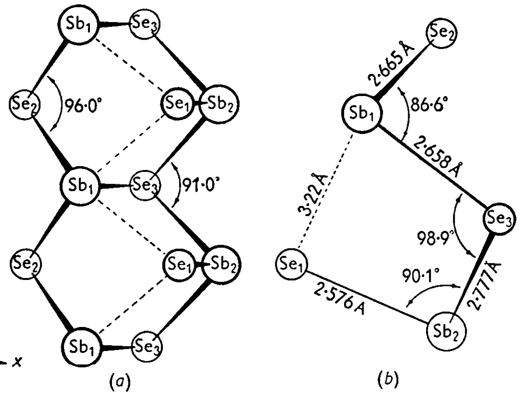
	B_{xx}	σB_{xx}	B_{xy}	σB_{xy}	B_{yy}	σB_{yy}
Sb_I	1·3	0·4	0·0	0·3	0·8	0·4
Sb_{II}	2·6	0·4	0·2	0·4	0·6	0·4
Se_I	0·8	0·4	−0·7	0·4	0·5	0·4
Se_{II}	1·3	0·5	−0·5	0·5	0·8	0·4
Se_{III}	1·3	0·4	−0·5	0·4	0·5	0·4

Table 4. *Observed and calculated structure factors F*(*hk*0)

h	k	F_o	F_c	h	k	F_o	F_c	h	k	F_o	F_c
0	2	106	99	4	7	171	−162	8	9	<12	4
0	4	49	− 37	4	8	99	91	8	10	19	− 20
0	6	127	127	4	9	154	−139	8	11	94	101
0	8	50	35	4	10	29	.29	8	12	58	66
0	10	126	−173	4	11	68	49	9	1	94	144
0	12	147	−176	4	12	41	42	9	2	<11	12
0	14	62	71	4	13	83	− 96	9	3	86	97
1	1	43	36	4	14	68	64	9	4	58	51
1	2	117	−146	5	1	90	− 93	9	5	17	11
1	3	131	−130	5	2	150	−210	9	6	145	154
1	4	90	80	5	3	171	−214	9	7	<12	− 6
1	5	29	24	5	4	92	71	9	8	54	− 46
1	6	88	− 84	5	5	31	21	9	9	23	− 6
1	7	30	− 23	5	6	177	182	9	10	37	41
1	8	50	− 43	5	7	12	− 3	9	11	58	− 61
1	9	90	− 98	5	8	64	− 61	9	12	19	13
1	10	123	−156	5	9	94	94	10	0	70	− 80
1	11	47	− 42	5	10	23	18	10	1	30	− 26
1	12	40	− 37	5	11	11	− 2	10	2	51	− 47
1	13	106	101	5	12	139	150	10	3	45	− 41
1	14	57	− 50	5	13	62	66	10	4	118	106
1	15	23	22	5	14	61	63	10	5	56	58
2	0	80	56	6	0	135	147	10	6	71	− 60
2	1	35	− 20	6	1	130	−141	10	7	44	− 34
2	2	90	− 66	6	2	104	87	10	8	73	− 67
2	3	203	244	6	3	<10	− 2	10	9	112	−110
2	4	214	−306	6	4	159	148	10	10	80	88
2	5	161	190	6	5	36	− 23	10	11	43	− 45
2	6	84	83	6	6	40	31	11	1	90	−107
2	7	103	117	6	7	87	− 81	11	2	73	36
2	8	107	109	6	8	35	− 32	11	3	62	− 72
2	9	94	108	6	9	<12	3	11	4	90	100
2	10	95	−113	6	10	15	− 9	11	5	21	− 19
2	11	54	45	6	11	85	73	11	6	19	20
2	12	47	46	6	12	55	− 54	11	7	47	− 39
2	13	18	10	6	13	78	87	11	8	76	70
2	14	56	71	7	1	50	44	11	9	104	103
3	1	115	108	7	2	153	−249	11	10	20	23
3	2	119	−126	7	3	<11	7	12	0	78	− 78
3	3	105	80	7	4	13	− 20	12	1	72	− 71
3	4	120	106	7	5	116	− 89	12	2	56	53
3	5	58	32	7	6	75	− 79	12	3	<12	13
3	6	195	233	7	7	30	25	12	4	95	84
3	7	176	189	7	8	145	−135	12	5	38	37
3	8	95	− 87	7	9	45	− 42	12	6	<12	8
3	9	72	− 68	7	10	124	−129	12	7	41	33
3	10	38	− 36	7	11	40	− 36	13	1	56	− 64
3	11	9	− 1	7	12	59	63	13	2	<12	− 1
3	12	40	41	7	13	28	− 20	13	3	54	46
3	13	8	7	8	0	123	−177	13	4	85	− 92
3	14	12	− 21	8	1	18	− 18	13	5	36	− 31
4	0	57	− 51	8	2	59	59	13	6	89	−118
4	1	56	40	8	3	18	13	13	7	10	18
4	2	128	−171	8	4	25	16	14	0	81	− 77
4	3	151	−136	8	5	147	130	14	1	17	10
4	4	160	−129	8	6	85	− 81	14	2	19	− 22
4	5	39	− 30	8	7	48	45	14	3	62	− 64
4	6	74	65	8	8	91	− 98				

Discussion of the structure

The present investigation confirms the structure reported by Hofmann for Sb_2S_3 in every important detail. Considering first only the strongest bonds (Sb–Se separations from 2·576 to 2·777 Å), the structure consists of infinite chains parallel to the *c* or needle axis. Projections of the structure of a chain on (010) and on (001) are shown in Fig. 2. Pairs of these chains are fastened together along 2_1 screw axes to form larger chains through sets of Sb–Se bonds of length 2·98 Å. These larger chains are, in turn, bonded into sheets roughly perpendicular to the *b* axis through sets of Sb–Se bonds, which are 3·26 Å in length. Finally, the sheets are held together to make the crystalline solid through two sets of Sb–Se 'bonds', which are 3·46 Å and 3·74 Å long respectively. For comparison, the sum of the van der Waals radii for Sb and Se is 4·20 Å. A projection of the structure on (001) is shown in Fig. 3.



(*a*) (*b*)

Fig. 2. Structure of the antimony selenide chain projected (*a*) on (010), (*b*) on (001).

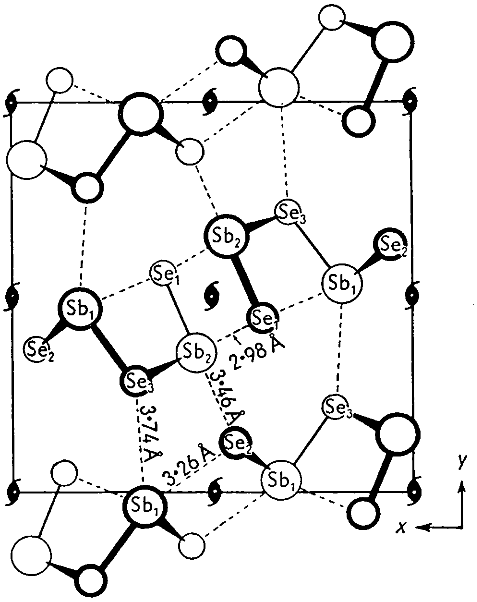


Fig. 3. Unit cell of antimony selenide projected on (001).

Because of the wide range of Sb–Se bond distances involved (Table 5), it has been of interest to apply Pauling's equation relating bond distance to bond number. This equation (Pauling, 1947),

$$D_n = D_1 - 0{\cdot}600 \log_{10} n \,,$$

relates the observed bond distance, D_n, to the single-bond distance, D_1, and the bond number, n. One of the main problems involved in applying this equation in the present case is the selection of the correct value for D_1. If one uses the single covalent bond radii given by Pauling (1940), then $D_1 = R_1(\mathrm{Sb}) + R_1(\mathrm{Se}) =$

Table 5. *Interatomic distances and bond angles in antimony triselenide*

Interatomic distances (σ = 0·025 Å)

Sb$_{II}$–Se$_{I}$	2·576 Å	(*a*)	Sb$_{I}$ –Se$_{II}$	3·260 Å	(*c*)
Sb$_{I}$ –Se$_{III}$	2·658	(*a*)	Sb$_{II}$–Se$_{II}$	3·465	(*d*)
Sb$_{I}$ –Se$_{II}$	2·665	(*a*)	Sb$_{I}$ –Se$_{III}$	3·743	(*d*)
Sb$_{II}$–Se$_{III}$	2·777	(*a*)	Se$_{II}$–Se$_{III}$	3·649	(*a*)
Sb$_{II}$–Se$_{I}$	2·984	(*b*)	Se$_{I}$ –Se$_{III}$	3·791	(*a*)
Sb$_{I}$ –Se$_{I}$	3·220	(*a*)	Sb$_{I}$ –Sb$_{II}$	4·130	(*a*)

Sb$_n$–Sb$'_n$ = Se$_n$–Se$'_n$ = c = 3·962 Å (*a*)

(*a*) Within same chain.
(*b*) Between nearest pairs of chains.
(*c*) Between next nearest pairs of chains (same sheet).
(*d*) Between chains in neighboring sheets.

Bond angles (σ = 1·3°)

Se$_{II}$ –Sb$_{I}$ –Se$_{III}$	86·6°	Sb$_{I}$ –Se$_{II}$ –Sb$_{I}$	96·0
Se$_{II}$ –Sb$_{I}$ –Se$_{II}$	96·0	Sb$_{II}$–Se$_{III}$–Sb$_{II}$	91·0
Se$_{I}$ –Sb$_{II}$–Se$_{III}$	90·1	Sb$_{I}$ –Se$_{III}$–Sb$_{II}$	98·9
Se$_{III}$–Sb$_{II}$–Se$_{III}$	91·0		

1·41+1·17 = 2·58 Å. However, there is some justification for using a somewhat larger radius for selenium (Marsh & McCullough, 1951; Goldish, Hedberg, Marsh & Schomaker, 1955). For this reason, two sets of bond numbers have been calculated, one based on D_1 = 2·58 Å and the other on D_1 = 2·63 Å. The results are given in Table 6. Regardless of which value of D_1 is considered, two interesting results are to be noted. One is the consistent values for the valence (Σn) for the atoms of a given kind, and the other is the 3:2 ratio between the calculated valences for Sb and Se. This second result is not independent of the first, however, as it is a necessary consequence of the first result and the stoichiometry. Use of the value D_1 = 2·63 Å has the advantage that the calculated valences are then closer to the expected chemical valences of the atoms involved. When correlated as above, the otherwise inconsistent appearing bond distances fall into a definite and reasonable pattern.

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Table 6. *Bond distances, bond numbers, and valences in antimony triselenide*

Central atom	Bonded atom	Distance and multiplicity	Bond number	
			D_1=2·58 Å	D_1=2·63 Å
Sb$_{I}$	Se$_{II}$	2·66 (2)	0·74 (2)	0·89 (2)
	Se$_{III}$	2·66 (1)	0·74 (1)	0·89 (1)
	Se$_{I}$	3·22 (2)	0·09 (2)	0·10 (2)
	Se$_{II}$	3·26 (1)	0·08 (1)	0·09 (1)
	Se$_{III}$	3·74 (1)	0·01 (1)	0·01 (1)
			Σ = 2·49	Σ = 2·97
Sb$_{II}$	Se$_{I}$	2·58 (1)	1·00 (1)	1·21 (1)
	Se$_{III}$	2·78 (2)	0·47 (2)	0·56 (2)
	Se$_{I}$	2·98 (2)	0·21 (2)	0·26 (2)
	Se$_{II}$	3·46 (2)	0·03 (2)	0·04 (2)
			Σ = 2·42	Σ = 2·93
Se$_{I}$	Sb$_{II}$	2·58 (1)	1·00 (1)	1·21 (1)
	Sb$_{II}$	2·98 (2)	0·21 (2)	0·26 (2)
	Sb$_{I}$	3·22 (2)	0·09 (2)	0·10 (2)
			Σ = 1·60	Σ = 1·93
Se$_{II}$	Sb$_{I}$	2·66 (2)	0·74 (2)	0·89 (2)
	Sb$_{I}$	3·26 (1)	0·08 (1)	0·09 (1)
	Sb$_{II}$	3·46 (2)	0·03 (2)	0·04 (2)
			Σ = 1·62	Σ = 1·95
Se$_{III}$	Sb$_{I}$	2·66 (1)	0·74 (1)	0·89 (1)
	Sb$_{II}$	2·78 (2)	0·47 (2)	0·56 (2)
	Sb$_{I}$	3·74 (1)	0·01 (1)	0·01 (1)
			Σ = 1·69	Σ = 2·02

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