

The Crystal Structure of CdSb and ZnSb

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Attempts to solve the crystal structure of the intermetallic compounds CdSb and ZnSb have previously been made by Halla and Adler¹, Halla, Nowotny and Tompa² and Ölander³. Of them, only Ölander was successful in approximately determining the dimensions of and the number of atoms in the elementary cell for CdSb, but without Weissenberg photographs a determination of the space group was difficult. The dimensions of the elementary cell given by Halla and coworkers do not agree at all with those given by Ölander or those found in this investigation and are certainly wrong. In an electrochemical investigation Ölander⁴ also found that at 240°—290° C there is not more than one stable intermediate phase in the Cd-Sb system between 16.0 and 86.5 atomic % Cd.

In this investigation the alloys were prepared by melting Cd (Zn) together with Sb in evacuated silica tubes in such proportions as to obtain alloys containing 50.0 atomic % Sb. The powder photographs of CdSb (Table 5) are those taken by Ölander³. Powder photographs of ZnSb (Table 6) were obtained from filings of the alloy, annealed at 400° C in evacuated silica tubes. The filings were allowed to cool rather slowly after the annealing. The powder photographs which were taken with Cr-K radiation in Phragmén focussing cameras, are very rich in lines, and it was not possible to determine the indices of the reflections until the structure was solved by means of Weissenberg photographs.

In order to obtain single crystals, small fragments of the alloy were annealed at 400° C in evacuated silica tubes for one week and allowed to cool rather slowly. The Weissenberg photographs of these fragments were very sharp, but in spite of taking photographs of several crystals it was not possible to avoid strong absorption effects in parts of them. There is no doubt that the absorption depends on the shape of the crystals used.

From the photographs it was found that the two compounds are isomorphous and orthorhombic with the following lattice dimensions:

	<i>a</i>	<i>b</i>	<i>c</i>
CdSb	6.471 Å (6.458 kX)	8.253 Å (8.236 kX)	8.526 Å (8.509 kX)
ZnSb	6.218 » (6.205 »)	7.741 » (7.725 »)	8.115 » (8.099 »)

If there are 16 atoms in the elementary cell the calculated density is 6.83 for CdSb and 6.36 for ZnSb. These values agree with the values given in the literature: 6.92 for CdSb¹ and 6.383 for ZnSb⁵. From the photographs the following three groups of systematic absences are found:

$$\begin{aligned} 0kl \text{ where } k \text{ is odd} \\ h0l \text{ where } l \text{ is odd} \\ hk0 \text{ where } h \text{ is odd} \end{aligned}$$

This is characteristic of the space group $D_{2h}^{15}-P/bca$.

In the attempts to solve the crystal structure, the structure problem of CdSb was attacked first. In this case, it was possible to calculate the intensities assuming all the atoms to be of the same kind, as the Cd and Sb atoms have nearly the same scattering power. From the intensity calculations it was easily found that the positions 4 (a) and 4 (b) of the space group could not be occupied by atoms. It therefore only remained to place both the Cd atoms and the Sb atoms in the eightfold position 8 (c), provided that D_{2h}^{15} is the correct space group. The parameter values were found by the method of trial and error. As the intensities of the reflections $h00$, $0k0$ and $00l$ are determined by only two unknown parameters it was possible to find probable but rather approximate values of the atomic coordinates from those reflections. Somewhat better values were obtained when the other reflections were taken into account.

Having obtained an approximately correct structure for CdSb, a more accurate evaluation of the atomic coordinates of ZnSb was made. In this case it was possible to distinguish between the two kinds of atoms. The structure cannot be disordered, because if it were, the intensities of the reflections would be approximately the same as in the photographs of CdSb Ölander's⁴ determination of the degree of disorder in CdSb confirms this statement. At 265° C the degree of disorder in CdSb amounts to $5 \cdot 10^{-3}$ %. After the atomic coordinates in ZnSb were ascertained a more exact determination of the parameters in CdSb was made. However, it was not possible to obtain perfect agreement between the observed and the calculated intensities for the reflections in the Weissenberg photographs (Tables 1—4). An attempt to refine

the parameters with Fourier projections was made, but the peaks were not sharp enough to allow a more accurate determination of the atomic coordinates than I had arrived at by means of the method of trial and error. There is no doubt that the discrepancies depend on the strong absorption mentioned above. However, the powder photographs (Tables 5—6) show a very good agreement between the observed and the calculated intensities.

The following parameter values were obtained:

	x_1	y_1	z_1	x_2	y_2	z_2
CdSb	0.136	0.072	0.108	0.456	0.119	— 0.128
ZnSb	0.142	0.081	0.111	0.461	0.103	— 0.122

Table 1. CdSb. Weissenberg photograph. Reflections $0kl$. Cu-K radiation.

l \ k	0	2	4	6	8	10
0		m 9.9	st 19.4	m 11.8	— 0.0	— 0.1
1		— 0.7	w 3.7	m 7.8	— 0.1	st ⁺ 8.4
2	vw 0.7	— 0.3	— 0.0	vw 0.3	vw 0.3	— 0.0
3		— 0.1	w ⁺ 6.9	m 8.1	vw 0.4	vst 11.1
4	vst 50.0	m 5.2	m ⁺ 13.6	m 8.5	— 0.0	
5		m ⁺ 2.9	— 0.2	m 4.7	— 0.0	
6	vw 2.4	w 1.2	— 0.0	m 1.8	st 2.1	
7		w 0.4	m ⁺ 5.7	m 6.2	w 0.4	
8	st 18.5	vw 1.6	m 7.3	m 3.6		
9		st 4.8	w 0.4			
10	m 2.8	m 1.6				

Table 2. CdSb. Weissenberg photograph. Reflections $h0l$. Cu-K radiation.

l \ h	0	2	4	6	8	10
0		vw 0.7	vst 50.0	vw 2.4	m 18.5	w 2.8
1		vw 4.4	w ⁺ 1.5	vw 1.2	m ⁻ 2.6	— 0.1
2	m 8.3	— 0.1	w 5.5	vw 0.3	w 3.3	w 0.4
3		— 0.4	vw 0.8	— 0.5	m ⁻ 1.6	w 0.9
4	m 3.5	vw 0.5	vw 2.0	w 2.8	vw 0.3	
5		st 28.2	vw 0.7	m ⁺ 17.6	m ⁻ 1.6	
6	vw 0.7	— 0.1	vw 0.5	w ⁺ 0.4		
7		m 7.9				
8	vw 0.4	vw 0.2				

Table 3. *ZnSb*. Weissenberg photograph. Reflections *0kl*. Cu-K radiation.

$l \backslash k$	0	2	4	6	8
0		st 9.6	st 11.0	st 17.6	vw 1.0
1		vw 0.5	m ⁻ 1.9	w 0.9	vw 0.2
2	w 0.8	vw 0.2	— 0.1	vw 0.3	vw 0.1
3		st ⁻ 1.7	m 3.5	vw 1.0	m 0.7
4	st 31.6	st 5.3	st 7.4	vst 13.3	vw 0.7
5		vw 0.0	vw 0.1	w 0.5	— 0.0
6	m 3.0	w 0.7	vw 0.6	m 1.8	st 0.4
7		m ⁺ 1.5	st 3.0	w 0.8	
8	st 11.5	m 1.4	m ⁺ 3.6	vwst 6.9	
9		m 0.5	w 0.1		
10	vst 4.0	st 1.0			

Table 4. *ZnSb*. Weissenberg photograph. Reflections *h0l*. Cu-K radiation.

$h \backslash l$	0	2	4	6	8	10
0		w 0.8	vst 31.6	m 3.0	vst 11.5	vst 4.0
1		st 7.7	m 0.9	m 2.8	st ⁻ 1.6	m 0.7
2	w 1.6	vw 0.01	m 0.9	w 0.03	w 0.6	m 0.03
3		vw 0.1	w 0.2	— 0.02	m 0.4	
4	st 4.1	w 0.2	st ⁻ 2.7	m 1.3	st ⁻ 1.0	
5		vst 17.2	m ⁻ 1.0	vwst 10.7	vwst 2.5	
6	m 3.0	vw 0.1	m ⁺ 2.3	m 0.5		
8		m 1.8				

In this table suffix 1 refers to Sb and suffix 2 to Cd and Zn. The accuracy of the parameter values amounts to ± 0.005 .

The intensities are calculated from the formula $I = p \cdot S^2$ where p is the frequency factor and S is the structure factor. β reflections have been omitted if they do not coincide with an α reflection. The following abbreviations are used in the tables: st = strong, m = medium, w = weak and v = very. Reflections in the powder photographs with $\sin^2\theta < 0.23$ must not be compared with reflections of higher glancing angles as the inner and the outer parts of the photographs are taken in different cameras.

As far as could be ascertained this type of crystal structure has not been found previously. Each atom is surrounded by four other atoms. One of them is of the same kind as the central atom, and the other three are of the

Table 5. CdSb. Powder photograph. Cr-K radiation.*

<i>hkl</i>	$\sin^2\Theta$ calc	$\sin^2\Theta$ obs	<i>I</i> obs	<i>I</i> calc	<i>hkl</i>	$\sin^2\Theta$ calc	$\sin^2\Theta$ obs	<i>I</i> obs	<i>I</i> calc
020	0.0771	0.0781	vw	18.7	024	0.3658	0.3672	m	{21.0 21.5
021	0.0951	—	—	2.3	133	0.3672			
112 β	0.1015	0.1023	m	{22.2 17.7	232	0.3709	0.3720	vw	5.0
102	0.1035				312	0.3735	—	—	0.4
112	0.1228	0.1237	st ⁺	111	321	0.3771	0.3784	m ⁺	69.2
200	0.1253	0.1253	w	14.8	042	0.3804	—	—	0.0
121	0.1264	0.1275	st	58.9	124	0.3972	0.3980	vw	3.7
210	0.1446	—	—	0.7	142	0.4118	—	—	0.5
022	0.1493	—	—	1.0	204	0.4141	0.4148	w	{22.5 1.4 0.4 2.4
211	0.1627	0.1642	st	88.2	400 β	0.4144			
122	0.1806	0.1819	w	24.2	115 β	0.4147			
202	0.1975	—	—	0.2	143 β	0.4149			
220	0.2024	—	—	0.1	410 β	0.4303	0.4335	m ⁻ (br)	{4.4 9.1 7.8
113	0.2130	0.2134	vw	5.9	323 β	0.4310			
212	0.2168	—	—	1.3	322	0.4313			
221	0.2205	0.2212	w	48.8	214	0.4334	—	—	0.4
131	0.2228	0.2241	vw	{29.8 4.8	240	0.4336	—	—	27.7
123 β	0.2238				241	0.4516	—	—	2.7
004 β	0.2393	0.2400	w	{19.1 0.4	233	0.4612	—	—	0.1
023	0.2395				125 β	0.4625	0.4645	m ⁻	{9.8 44.2
041 β	0.2704	0.2717	w	{2.9 24.2	313	0.4637			
123	0.2708				043	0.4707	0.4715	w ⁺	{28.9 0.6
222	0.2746	—	—	0.1	304 β	0.4718			
132	0.2769	0.2777	st ⁺	198	331	0.4735	—	—	1.8
004	0.2888	0.2895	st ⁻	95.4	224	0.4912	—	—	0.1
230	0.2987	0.2995	w	18.9	215 β	0.4924	0.4950	w	{4.4 0.6
232 β	0.3066	—	—	1.0	243 β	0.4926			
213	0.3073	0.3079	st	{119 36.5	421 β	0.4930	0.4950	w	{10.1 11.1
040	0.3083				044 β	0.4934			
231	0.3168	—	—	1.0	134	0.4935	—	—	4.2
311	0.3193	0.3200	st	{89.2 5.9	400	0.5014	0.5026	w ⁺ (br)	{7.2 9.1
104	0.3201				250 β	0.5017			
041	0.3263	0.3272	w	14.6	115	0.5018	0.5026	w ⁺ (br)	{2.2 12.1
114	0.3394	—	—	0.6	143	0.5020			
302	0.3542	0.3551	vw	{1.3 1.6	341 β	0.5028	—	—	3.9
322 β	0.3565				242	0.5058	—	—	0.1
141	0.3576	0.3590	m ⁻	{35.6 5.5	410	0.5206	0.5215	m	{21.9 45.7
240 β	0.3584				323	0.5215			
223	0.3648	0.3657	m	41.2	332	0.5276	0.5286	w	{9.3 11.6
					025	0.5282			

* In the powder photographs of CdSb it has been impossible to identify the following three lines: 0.2598 (vw), 0.2836 (vw) and 0.4197 (vw).

<i>hkl</i>	$\sin^2\theta$ calc	$\sin^2\theta$ obs	<i>I</i> obs	<i>I</i> calc	<i>hkl</i>	$\sin^2\theta$ calc	$\sin^2\theta$ obs	<i>I</i> obs	<i>I</i> calc	
151	0.5310	—	—	3.0	333	0.6178	—	—	3.7	
411	0.5387	—	—	7.2	251	0.6250	0.6250	m-	39.4	
430 β	0.5577	0.5593	m	6.8	144	0.6283	—	—	0.7	
153 β	0.5582				1.9	324	0.6478	—	—	1.7
125	0.5596	0.5711	vw	48.8	006	0.6497	—	—	4.9	
304	0.5708				3.2	422	0.6506	—	—	1.2
431 β	0.5726				2.7	404 β	0.6530	0.6540	m	1.7
060 β	0.5733				4.9	225	0.6536			
402	0.5735	0.5804	vw	2.0	145 β	0.6536	—	7.8		
420	0.5784				14.1	135	0.6559	19.7		
116 β	0.5788	—	—	0.0	342	0.6625	0.6624	w	24.5	
152	0.5852				11.1	154 β		0.6626	0.8	
234	0.5875	0.5886	w	22.1	430	0.6748	0.6747	w	33.9	
061 β	0.5881				6.4	153		0.6754	9.7	
314	0.5900	—	—	2.8	252	0.6792	—	—	1.8	
412	0.5928	—	—	0.0	106	0.6810	—	—	5.1	
215	0.5958	0.5966	st	21.8	413	0.6830	0.6846	vw	2.7	
243	0.5960				3.2	441 β				0.6841
421	0.5965				50.4	431	0.6928	0.6929	w ⁺	13.3
044	0.5970				55.4	060	0.6936			
244 β	0.5970	0.6072	m	8.5	116	0.7003	0.7000	w ⁺	55.3	
250	0.6070				45.7					
341	0.6083				19.5					

second kind. The four surrounding atoms form a deformed tetrahedron. It is possible to regard the lattice as a very strongly deformed diamond lattice. The interatomic distances may be seen from the following table:

CdSb		ZnSb	
Cd — Cd	2.99 kX	Zn — Zn	2.58 kX
Cd — Sb	2.80 »	Zn — Sb	2.66 »
	2.81 »		2.69 »
	2.91 »		2.74 »
Sb — Sb	2.81 »	Sb — Sb	2.81 »

These distances seem to be plausible. If the coordination number is assumed to be four, the following distances can be calculated by Pauling's ⁶ method:

Cd — Cd	2.80 kX	Zn — Zn	2.57 kX
Cd — Sb	2.85 kX	Zn — Sb	2.67 kX
	Sb — Sb	2.89 kX	

Table 6. *ZnSb. Powder photograph. Cr-K radiation.*

<i>hkl</i>	$\sin^2\Theta$ calc	$\sin^2\Theta$ obs	<i>I</i> obs	<i>I</i> calc	<i>hkl</i>	$\sin^2\Theta$ calc	$\sin^2\Theta$ obs	<i>I</i> obs	<i>I</i> calc		
020	0.0876	0.0862	vw	18.3	232	0.4123	0.4142	m	{ 2.7 29.8		
021	0.1076	—	—	2.1	321	0.4132		—		—	
102	0.1137	0.1132	w	28.7	042	0.4303	—	—	0.2		
112	0.1356	0.1350	m	{ 53.6 2.8	124	0.4405	—	—	1.8		
200	0.1358				204	0.4548	—	—	3.8		
121	0.1415	0.1405	w	48.8	142	0.4643	0.4642	vvw	4.9		
210	0.1577	—	—	6.7	322	0.4730	—	—	1.8		
022	0.1674	—	—	1.0	214	0.4767	0.4761	vvw	8.2		
211	0.1777	0.1778	w	60.9	240	0.4864	—	—	4.7		
122	0.2013	0.2014	vw	{ 17.1 4.6	241	0.5063	0.5094	w	{ 8.0 34.0		
221 β	0.2016				313	0.5069				233	0.5124
202	0.2156	—	—	0.0	331	0.5228	—	—	0.4		
220	0.2235	—	—	0.0	043	0.5300	0.5304	vw	14.7		
113	0.2353	—	—	0.0	224	0.5424	—	—	0.2		
212	0.2375	—	—	0.7	400	0.5433	—	—	8.5		
221	0.2434	0.2440	m	22.8	134	0.5501	0.5511	vw	{ 5.8 2.0		
123 β	0.2493	0.2503	vw	{ 3.8 3.0	243 β	0.5514				115	0.5542
131	0.2511				044 β	0.5544	143	0.5639	0.5641	vw	13.5
023	0.2670	0.2681	vvw	7.3	410	0.5653	0.5675	vw	{ 9.5 0.0		
123	0.3010	0.3020	w	19.0	242	0.5661				250 β	0.5661
222	0.3032	—	—	0.0	323	0.5727	0.5739	vw	13.7		
132	0.3109	0.3116	vst	136	332	0.5826	0.5828	w	{ 22.4 4.7		
004	0.3189	0.3208	m	59.8	251 β	0.5826				143 β	0.5826
230	0.3330	0.3335	m ⁻	{ 29.6 5.0	411	0.5852	—	—	0.0		
223 β	0.3337				323	0.5727	0.5739	vw	13.7		
141 β	0.3350	0.3380	st	{ 6.9 4.2	312	0.5826	0.5828	w	{ 22.4 4.7		
024 β	0.3367				413 β	0.5826				411	0.5852
213	0.3372	0.3380	st	{ 85.0 0.7	025	0.5860	—	—	0.1		
312 β	0.3373				151	0.6016	—	—	0.0		
311	0.3475	0.3495	st	{ 72.9 21.4	125	0.6199	0.6216	w	{ 43.8 1.0		
040	0.3506				402	0.6231				304	0.6246
104	0.3529	—	—	3.5	420	0.6310	—	—	6.7		
231	0.3530	—	—	0.1	412	0.6450	—	—	0.2		
041	0.3705	0.3706	vvw	7.5	314	0.6465	—	—	1.4		
114	0.3748	—	—	1.7	421	0.6509	0.6529	m	{ 40.1 38.7		
302	0.3854	—	—	0.4	234	0.6520				215	0.6561
240 β	0.4023	0.4040	m	{ 0.9 24.8	314	0.6465	—	—	—		
223	0.4029				421	0.6509	0.6529	m	40.1		
141	0.4045	0.4074	vw	{ 34.6 21.2	234	0.6520	—	—	8.0		
024	0.4066				312	0.4073	3.5	152	0.6614	—	—
133	0.4106	—	—	2.0	341	0.6761	—	—	0.4		
243	0.6658	—	—	9.9	333	0.6822	—	—	13.7		
044	0.6695	0.6695	w	{ 30.1 0.7	250	0.6836	0.6848	vw	{ 13.7 13.5		
061 β	0.6697				315 β	0.6840					

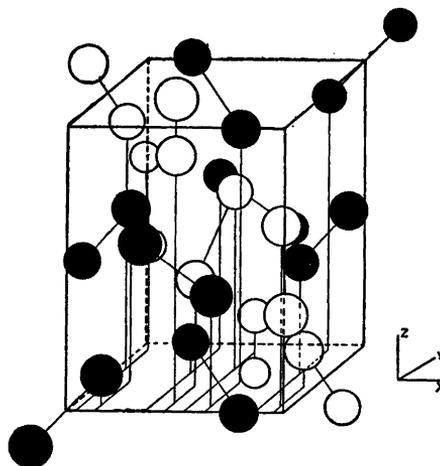


Fig. 1. The crystal structure of CdSb and ZnSb. ● Sb, ○ Cd or Zn.

Only the distance between the Cd atoms in CdSb differs rather much from the calculated value.

The structure is reproduced in Fig. 1.

SUMMARY

The intermetallic compounds CdSb and ZnSb are isomorphous, crystallize in the space group $D_{2h}^{15} - P/bca$, and their orthorhombic cells contain eight formula units. The lattice dimensions, the atomic coordinates and the interatomic distances are determined and may be seen from the tables in the text.

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REFERENCES

1. Halla, F., and Adler, J. *Z. anorg. u. allgem. Chem.* **185** (1928) 184.
2. Halla, F., Nowotny, H., and Tompa, H. *Z. anorg. u. allgem. Chem.* **214** (1933) 196.
3. Ölander, A. *Z. Krist.* **91** (1935) 243.
4. Ölander, A. *Z. physik. Chem. A* **173** (1935) 284.
5. Cooke, A. *Am. J. Sci. (Sill.)* **2**, **18** (1855) 234, **20** (1855) 212.
6. Pauling, L. *J. Am. Chem. Soc.* **69** (1947) 542.

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