tion of these bonds is 0·0033 Å. According to Cruick-shank (1949), if the difference between two bonds is more than three times the standard deviation of the distance, this difference is real. It is therefore concluded that the difference in the As–As bond lengths is statistically significant. This alternation of bond lengths in chains of like atoms is not unusual. It has been observed in many aliphatic carbon compounds and in the sulfur chains of Cs_2S_6 (Abrahams & Grison, 1953). The As–As distances are close to the single bond distances found in the crystalline element (Neuberger, 1933) and in As_4 vapor (Allen & Sutton, 1950).

One can think of the lithium atoms as being in spirals coaxial with the arsenic spirals, with the spiral rotated approximately 90° and the spiral radius somewhat larger. Each atom has six neighbors of the other kind at the corners of a deformed octahedron. The average of all twelve Li–As distances is 2·78 Å. Li_1 has eight lithium neighbors at distances ranging from 3·00 to 3·78 Å for an average of 3·49 Å. Li_2 has seven lithium neighbors at distances ranging from 2·99 to 3·78 Å for an average of 3·39 Å. The average non-bonded As–As distance is 4·03 Å.

The chemical bonding in LiAs appears to be a combination of covalent As–As bonds and metallic Li–As and Li–Li bonds. The As–As bonds in the spiral chain are certainly covalent single bonds. The presence of metallic bonds are indicated by the physical properties. The crystals have a metallic lustre and a large piece of LiAs showed electrical conductivity in a qualitative test.

I wish to thank R. E. Tate and F. W. Schonfeld for supplying the LiAs crystals and R. B. Roof, Jr., for drawing Fig. 4. Various portions of the necessary computing were done on the IBM CPC, IBM 704, Maniac I and Maniac II. I am indebted to many members of the LASL computer groups for programming assistance.

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The Crystal Structure of NaSb*

BY DON T. CROMER

University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico, U.S.A.

The crystal structure of NaSb has been determined by single crystal methods and found to be isostructural with LiAs. The dimensions of the monoclinic cell are $a = 6·80±0·02$, $b = 6·34±0·02$, $c = 12·48±0·04$ Å, and $\beta = 117·6±0·2°$. The parameters were determined by least-squares refinement of the $h0l$ and $0kl$ zones with all cross-products included. An interesting feature of this structure is that one of the Na–Na distances is 3·44±0·09 Å, significantly shorter than in metallic sodium.

Introduction

The compound NaSb has been described by Zintl & Dullenkopf (1932), who reported it to be monoclinic. However, they did not give the cell dimensions. The present structure determination of NaSb was undertaken in the hope that it would be isostructural with LiAs (Cromer, 1959), as indeed it is. Knowledge of the sodium positions in NaSb would have been useful in placing the lithium atoms in LiAs, but because the

LiAs structure was finally determined on the basis of its diffraction data alone, the NaSb structure is being reported separately.

Experimental

A specimen of NaSb was prepared in the following manner. A stoichiometric mixture of sodium and antimony was placed in a silica tube which was evacuated and then filled with dry argon. The tube was heated to 650 °C. and slowly cooled. Then the tube was opened in a dry box filled with dry nitrogen

Table 1. *Results of least-squares refinement of* NaSb

	x	y	z(h0l)	z(0kl)	z (average)
Sb_1	$0\cdot3076\pm0\cdot0010$	$0\cdot8994\pm0\cdot0007$	$0\cdot2951\pm0\cdot0005$	$0\cdot2956\pm0\cdot0005$	$0\cdot2954\pm0\cdot0004$
Sb_2	$0\cdot2932\pm0\cdot0010$	$0\cdot1599\pm0\cdot0008$	$0\cdot1056\pm0\cdot0006$	$0\cdot1047\pm0\cdot0005$	$0\cdot1051\pm0\cdot0004$
Na_1	$0\cdot2108\pm0\cdot0069$	$0\cdot3892\pm0\cdot0055$	$0\cdot3212\pm0\cdot0036$	$0\cdot3274\pm0\cdot0028$	$0\cdot3251\pm0\cdot0022$
Na_2	$0\cdot2179\pm0\cdot0070$	$0\cdot6725\pm0\cdot0056$	$0\cdot0399\pm0\cdot0039$	$0\cdot0414\pm0\cdot0027$	$0\cdot0409\pm0\cdot0022$

and the compound removed. Microscopic examination of the compound that had been formed revealed the presence of only a single phase. Needle-like single crystals were obtained and were sealed within thin-walled glass capillaries. Mineral oil was used to moisten the crystals so that they would adhere to the walls of the capillaries. Before removing the capillaries from the drybox their open ends were sealed by touching them to an electrically heated wire. The metallic luster of these crystals and their good cleavage parallel to the needle axis as well as their equally good cleavage on any of a number of $h0l$ faces were characteristics similar to those of LiAs crystals. NaSb crystals were mounted so that they could be rotated about the needle axis, and zero-level Weissenberg photographs were taken. These photographs had the same pseudo-symmetry possessed by $h0l$ Weissenberg photographs of LiAs and showed the two compounds to be isostructural. The space group is $P2_1/c$ with

$$a = 6\cdot80\pm0\cdot02, \quad b = 6\cdot34\pm0\cdot02, \quad c = 12\cdot48\pm0\cdot04 \text{ Å};$$
$$\beta = 117\cdot6\pm0\cdot2° \ .$$

The dimensions a and c were determined from resolved α_1, α_2 doublets on zero-level Weissenberg photographs (Cu $K\alpha_1$ $\lambda = 1\cdot5405$ Å). The b axis was measured on a precession photograph (Mo $K\alpha$ $\lambda = 0\cdot7107$ Å). The density of NaSb was not experimentally determined but eight formula units per unit cell were assumed because of its relation to LiAs. The calculated density is $4\cdot03$ g.cm.$^{-3}$.

For intensity measurements Mo $K\alpha$ radiation was used and a crystal having the dimensions $0\cdot04\times0\cdot08\times0\cdot34$ mm. was selected and mounted so that the long dimension was parallel to the rotation axis. The $h0l$ intensities were measured with a Geiger counter attachment on a Weissenberg camera (Evans, 1953). The $0kl$ intensities, from the same crystal, were estimated by eye from a series of timed exposures made with a precession camera. For the precession data the Lp corrections of Waser (1951) were applied. The 100, 002, and $10\bar{2}$ reflections were not recorded with the Geiger counter because they were obscured by the beam trap.

Determination of the structure

Fourier projections on 100 and 010 were computed. Phases from the corresponding LiAs structure factors were used. Resolution was complete in the 100 projection and the sodium atoms were clearly visible. There was some overlap in the 010 projection but the sodium atoms were again visible.

Refinement of these projections was made by least-squares, and the 010 projection was refined first. Included as parameters were the scale factor, an isotropic temperature factor for each chemical species, and the eight atomic coordinates. All cross-products were included in the eleven parameter problem. The final temperature factors were $B_{Na} = 2\cdot20\pm0\cdot60$ and $B_{Sb} = 1\cdot34\pm0\cdot09$ Å^2. The results for the atomic coordinates are given in Table 1.

For the 100 projection the form factors were first modified by the temperature factors which had been determined from the $h0l$ zone. Only the scale factor and the eight atomic coordinates were included as parameters. These results are also given in Table 1. With the exception of z_{Na_1} the agreement between independent determinations of the z parameters is
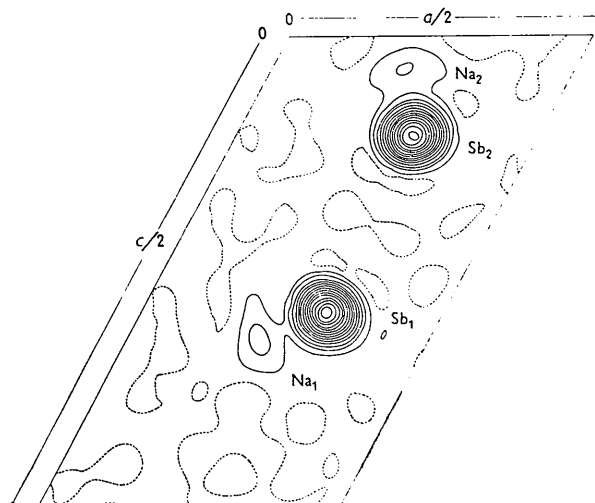

Fig. 1. Projection of NaSb on 010. The zero contour is dashed. The contours are at equal intervals of 10 e.Å^{-2}.
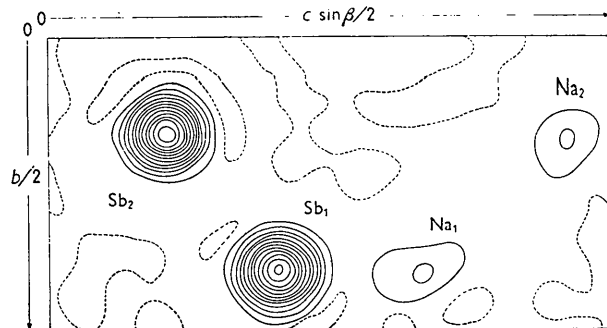

Fig. 2. Projection of NaSb on 100. The zero contour is dashed The contours are at equal intervals of 10 e.Å^{-2}.

Table 2. *Observed and calculated structure factors for* NaSb

h k	l	$F_{obs.}$	$F_{calc.}$
0 0	2	97	−97
0 0	4	71	−65
0 0	6	54	−44
0 0	8	32	−33
0 0	10	142	143
0 0	12	72	−67
0 0	14	39	−25
0 0	16	28	−22
1 0	0	98	−96
1 0	2	37	−21
1 0	4	213	−217
1 0	6	187	189
1 0	8	18	8
1 0	10	62	−61
1 0	12	16	−16
1 0	14	22	−36
1 0	16	60	65
1 0	−2	110	109
1 0	−4	280	285
1 0	−6	191	−176
1 0	−8	10	−2
1 0	−10	30	−30
1 0	−12	85	69
1 0	−14	48	43
1 0	−16	70	−69
2 0	0	278	−314
2 0	2	79	76
2 0	4	137	131
2 0	6	71	−72
2 0	8	0	19
2 0	10	90	−97
2 0	12	53	57
2 0	14	43	42
2 0	−2	40	29
2 0	−4	64	−45
2 0	−6	191	186
2 0	−8	22	20
2 0	−10	128	−114
2 0	−12	37	32
2 0	−14	0	−5
2 0	−16	74	74
2 0	−18	29	−26
3 0	0	190	181
3 0	2	27	−24
3 0	4	74	70
3 0	6	111	−110
3 0	8	26	−18
3 0	10	90	96
3 0	12	15	−16
3 0	−2	141	−135
3 0	−4	191	−183
3 0	−6	62	44
3 0	−8	15	15
3 0	−10	126	121
3 0	−12	122	−104
3 0	−14	27	−24
3 0	−16	30	32
4 0	0	104	88
4 0	2	25	−30
4 0	4	126	−118
4 0	6	93	99
4 0	8	14	5
4 0	10	19	28
4 0	12	28	−28
4 0	−2	52	52
4 0	−4	106	88
4 0	−6	216	−217
4 0	−8	19	2
4 0	−10	32	24
4 0	−12	30	35

h k	l	$F_{obs.}$	$F_{calc.}$
4 0	−14	28	28
4 0	−16	102	−99
4 0	−18	28	31
5 0	0	156	−146
5 0	2	14	21
5 0	4	23	33
5 0	6	32	28
5 0	8	15	15
5 0	10	71	−76
5 0	12	17	20
5 0	−2	95	90
5 0	−4	58	49
5 0	−6	86	81
5 0	−8	34	−35
5 0	−10	137	−140
5 0	−12	104	87
5 0	−14	0	−3
5 0	−16	27	27
5 0	−18	26	−28
6 0	0	55	40
6 0	2	0	5
6 0	4	64	66
6 0	6	66	−71
6 0	8	21	−20
6 0	−2	89	−83
6 0	−4	73	−66
6 0	−6	133	137
6 0	−8	0	−4
6 0	−10	61	55
6 0	−12	95	−86
6 0	−14	30	−29
6 0	−16	78	76
6 0	−18	16	−17
7 0	0	82	74
7 0	2	0	−6
7 0	4	56	−65
7 0	6	0	15
7 0	−2	30	−27
7 0	−4	0	19
7 0	−6	125	−121
7 0	−8	44	41
7 0	−10	77	89
7 0	−12	34	−29
7 0	−14	32	15
7 0	−16	69	−65
7 0	−18	37	35
8 0	0	64	−72
8 0	2	0	0
8 0	4	0	−13
8 0	6	29	31
8 0	−2	74	70
8 0	−4	19	29
8 0	−6	41	−40
8 0	−8	17	−10
8 0	−10	81	−77
8 0	−12	91	87
9 0	0	25	−14
9 0	−2	27	−16
9 0	−4	23	−30
9 0	−6	94	93
9 0	−8	41	−28
9 0	−10	0	−27
9 0	−12	0	−23
9 0	−14	0	−11
9 0	−16	61	63
9 0	−18	41	−26
10 0	0	44	51
10 0	−2	37	−36
10 0	−4	0	−3
10 0	−6	0	−19

h k	l	$F_{obs.}$	$F_{calc.}$
10 0	−8	0	21
10 0	−10	55	55
10 0	−12	58	−51
0 2	0	28	−33
0 4	0	183	−192
0 6	0	17	18
0 8	0	0	8
0 1	1	42	32
0 2	1	89	79
0 3	1	87	−74
0 4	1	127	126
0 5	1	33	32
0 6	1	33	−41
0 7	1	33	39
0 8	1	79	−79
0 0	2	104	−97
0 1	2	171	−162
0 2	2	82	−74
0 3	2	68	−67
0 4	2	65	63
0 5	2	75	74
0 6	2	80	79
0 7	2	17	−11
0 8	2	0	−21
0 1	3	33	27
0 2	3	230	−233
0 3	3	56	48
0 4	3	47	46
0 5	3	61	−70
0 6	3	42	45
0 7	3	28	−32
0 8	3	14	−15
0 0	4	75	−65
0 1	4	26	24
0 2	4	61	58
0 3	4	75	74
0 4	4	28	24
0 5	4	33	33
0 6	4	59	−76
0 7	4	59	−57
0 8	4	0	11
0 1	5	192	−169
0 2	5	0	−1
0 3	5	146	141
0 4	5	0	6
0 5	5	45	45
0 6	5	0	−5
0 7	5	31	−24
0 8	5	0	0
0 0	6	54	−44
0 1	6	31	29
0 2	6	47	41
0 3	6	75	−83
0 4	6	23	16
0 5	6	54	−60
0 6	6	47	−52
0 7	6	59	79
0 1	7	79	80
0 2	7	132	136
0 3	7	26	−23
0 4	7	31	−28
0 5	7	61	−66
0 6	7	31	−37
0 7	7	21	−16
0 0	8	33	−33
0 1	8	135	133
0 2	8	42	−37
0 3	8	73	75

Table 2 (cont.)

h k	l	$F_{obs.}$	$F_{calc.}$		h k	l	$F_{obs.}$	$F_{calc.}$		h k	l	$F_{obs.}$	$F_{calc.}$
0 4	8	0	24		0 3	10	28	−30		0 4	12	33	40
0 5	8	65	−60		0 4	10	79	−84		0 5	12	37	42
0 6	8	54	57		0 5	10	0	16		0 1	13	0	6
0 7	8	0	−6		0 6	10	0	4		0 2	13	68	−72
0 1	9	0	1		0 1	11	31	32		0 3	13	28	20
0 2	9	51	−55		0 2	11	0	8		0 4	13	0	5
0 3	9	59	−61		0 3	11	42	−45		0 0	14	37	−25
0 4	9	45	−46		0 4	11	61	69		0 1	14	0	13
0 5	9	54	58		0 5	11	0	7		0 2	14	31	31
0 6	9	0	23		0 6	11	0	−16		0 3	14	31	32
0 7	9	26	36		0 0	12	61	−67		0 1	15	45	−53
0 0	10	141	143		0 1	12	59	−60		0 2	15	28	33
0 1	10	37	−36		0 2	12	0	−11					
0 2	10	0	−4		0 3	12	17	−19					

excellent, and the difference between the two values of z_{Na_1} is not statistically significant.

Form factors were taken from the *Internationale Tabellen* (1935). The antimony form factor was reduced by 1·2 electrons to correct for anomalous dispersion (James, 1948). For the $h0l$ zone $R = 8·9\%$ and for the $0kl$ zone, $R = 8·3\%$, where terms with $F_{obs.} = 0$ have been omitted in both cases. All observations were given equal weight. The observed and calculated structure factors are given in Table 2.

A few of the structure factor signs of NaSb differ from those of LiAs. The two Fourier projections were therefore recalculated with all signs taken from the least-squares refinement. Computed amplitudes of the 100, 200 and $10\bar{2}$ reflections were included in the 010 projection. These Fouriers are shown in Figs. 1 and 2 and coordinates therefrom are given in Table 3.

Table 3. Atomic coordinates of NaSb from Fourier projections

	x	y	z(h0l)	z(0kl)
Sb_1	0·3052	0·9016	0·2935	0·2948
Sb_2	0·2936	0·1586	0·1066	0·1057
Na_1	0·2210	0·4048	0·3227	0·3309
Na_2	0·2190	0·6680	0·0346	0·0397

Peak positions were determined by a least-squares fit of the electron densities near the peaks to a 6 parameter Gaussian function (Shoemaker et al., 1950).

Accuracy of the least-squares refinement

The standard deviation of a variable in a least-squares refinement can be expressed as

$$\sigma(\xi_i) = \left[\frac{\Sigma(\Delta F)^2}{(m-s)} \cdot D_{ii} \right]^{\frac{1}{2}},$$

where D_{ii} is the ith diagonal element of the matrix which is inverse to matrix M of the coefficients of the normal equations, m is the number of observations, s is the number of variables and ΔF has its usual significance. This expression was used in these problems.

In many least-squares refinements of crystal struc-

tures the assumption has been made that off-diagonal terms can be neglected, particularly for products involving different atoms and even for products involving the same atom if the cell is orthogonal, or nearly so. When all the coefficients of the normal equations have not been calculated one cannot use the inverse matrix to determine the error. It is common practice (for example, see Shoemaker et al., 1950) to make the assumption that, because the off-diagonal terms are relatively small, the diagonal terms of D are approximately equal to the reciprocals of the diagonals of M. A different approach to this problem, which is applicable where one of the atoms is considerably heavier than the others, has been used by Blackmore & Abrahams (1955).

Now we may test the validity of this assumption on a practical example. For the $0kl$ zone, which is an orthogonal projection, the approximation $1/M_{ii}$ to the true inverse D_{ii} was found to be accurate to better than 1%. For the $h0l$ zone, which is non-orthogonal ($\beta = 117·6°$), the approximation underestimates the standard deviations of the atomic coordinates by 12 to 22%. Hence, the approximation appears fully justified for an orthogonal system but it is not necessarily true that the above results can be applied to other structures. They do suggest, however, that one should increase the approximate standard deviations

Table 4. Interatomic distances in NaSb

The standard deviation for Sb–Sb distances is 0·014; for Na–Sb distances, 0·06, and for Na–Na distances, 0·09 Å

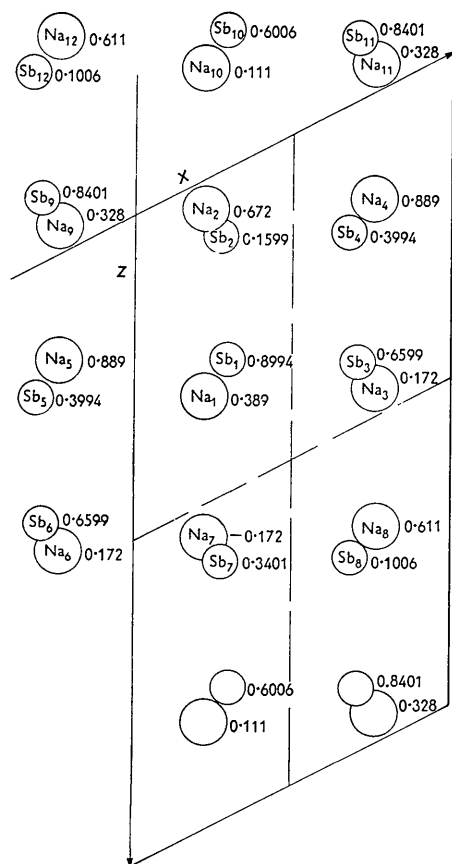|	d			d
Sb_1–Sb_2(+)	2·857 Å		Na_1–Na_3	3·71 Å
–Sb_3	2·845		–Na_7	4·45
Na_1–Sb_1	3·36		–Na_7(+)	3·85
–Sb_1(−)	3·23		–Na_6	4·21
–Sb_3	3·52		–Na_5	4·10
–Sb_5	3·13		–Na_5(−)	4·10
–Sb_7	3·29		–Na_2	4·00
–Sb_2	3·38		–Na_9	4·14
Na_2–Sb_2	3·33		Na_2–Na_5	4·21
–Sb_2(+)	3·17		–Na_9	3·44
–Sb_9	3·26		–Na_{10}	4·45
–Sb_4	3·39		–Na_{10}(+)	3·85
–Sb_{10}	3·42		–Na_4	3·71
–Sb_1	3·28		–Na_{12}	4·14

Fig. 3. Projection of the structure of NaSb on 010.
The y coordinate is given beside each atom.

by a factor varying from 0% for $\beta = 90°$ to about 25% for $\beta = 120°$.

Discussion of the structure

The general features of the structure are essentially the same as those described for LiAs. The atomic coordinates differ very little in the two compounds.

The various interatomic distances are tabulated in Table 4 in the same form and order in which those of LiAs were tabulated. The structure in projection on 010 is shown in Fig. 3. The average of the twelve Na–Sb distances is 3·31 Å. Na_1 has eight sodium neighbors at an average distance of 4·07 Å and Na_2 has seven sodium neighbors at an average distance of 3·97 Å.

An interesting feature of this structure is the close approach between Na_2 and Na_9 through the center of symmetry. This distance is 3·44 Å and is significantly shorter than the smallest interatomic distance of 3·71 Å in metallic sodium. Within the accuracy of this analysis, the two Sb–Sb bonds are of equal length and compare favorably with the shortest Sb–Sb distance of 2·87 Å in metallic Sb (Wyckoff, 1948).

The least-squares refinements and initial Fourier projections were computed on Maniac I. The IBM 704 was used to compute a final set of structure factors and the final Fourier projections.

I wish to thank Mr A. E. Gorum for preparing the crystals of NaSb, and Mr R. L. Bivins for assistance in coding the least-squares problems for Maniac I.

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