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The Crystal Structure of LiAs*

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The crystal structure of LiAs has been determined by single-crystal methods. The approximate structure was deduced from photographic data, and a least-squares refinement was made with data obtained with a scintillation counter. LiAs is monoclinic with eight formula units in space group $P2_1/c$. The cell dimensions are $a=5\cdot79\pm0\cdot01$, $b=5\cdot24\pm0\cdot01$, $c=10\cdot70\pm0\cdot02$ Å, and $\beta=117\cdot4\pm0\cdot2°$. The arsenic atoms form singly bonded infinite spiral chains parallel to the b axis. The As–As bonds differ slightly in length and are alternately 2·454 and 2·472 Å. The average Li–As distance is 2·78 Å. The lithium atoms are in positions defined approximately by a spiral coaxial with the arsenic chains but with a somewhat larger radius and the spiral rotated approximately 90°. Each atom has six neighbors of the other kind at the corners of a deformed octahedron.

Introduction

In a study of the phase-equilibrium relationships in a portion of the lithium-arsenic system a compound of the composition LiAs was found. Because this was a new and interesting compound a detailed structure investigation was undertaken. During the course of this work the isostructural compound NaSb was investigated in order to place the lithium atoms of LiAs by analogy with the corresponding sodium positions of NaSb. Ultimately, the lithium atoms were found directly from the diffraction data with an accuracy probably greater than if they had been located by isomorphous substitution. The results of the analysis of the NaSb structure are, therefore, being reported separately (Cromer, 1959).

Experimental

The compound LiAs was prepared by R. E. Tate and F. W. Schonfeld (Tate & Schonfeld, 1958) by reacting a stoichiometric mixture of lithium and arsenic in a closed bomb. Chemical analysis of the reaction product was very difficult, but results indicated that the product had a composition of from 45 to 50 atomic% arsenic. The principal evidence for that composition is that all of the reactants were consumed, and microscopic examination revealed the presence of only a single phase. Tate & Schonfeld (1958) experimentally determined the density of LiAs to be 3·5 g.cm.$^{-3}$ by displacement in bromobenzene. All manipulations of LiAs were performed in a drybox flushed and filled with dry nitrogen. It is of interest to note that, although lithium metal reacts with nitrogen, freshly cleaned surfaces of LiAs remained bright and shiny for periods of several hours in the dry nitrogen atmosphere.

A specimen of the compound was crushed and among the fragments were found many needle-like single crystals. The crystals were moistened with mineral oil and placed in thin-walled glass capillaries. The mineral oil was used so that the crystals would adhere to the capillary walls. Before the capillaries were removed from the drybox they were sealed by touching their open ends to an electrically heated wire.

Weissenberg and precession photographs were taken and the systematic extinctions uniquely established the space group to be $P2_1/c$. The cell dimensions were determined by measuring resolved α_1, α_2-doublets on zero-layer Weissenberg films. The cell dimensions are

$$a = 5\cdot79\pm0\cdot01,\quad b = 5\cdot24\pm0\cdot01,\quad c = 10\cdot70\pm0\cdot02\ \text{Å}\ ,$$
$$\beta = 117\cdot4\pm0\cdot2°\quad (\text{Cu}\ K\alpha_1,\ \lambda = 1\cdot5405\ \text{Å}).$$

The calculated density with $Z = 8$ is 3·68 g.cm.$^{-3}$. In view of the experimental difficulty of measuring the density of this reactive compound, the agreement between the experimental and calculated density is considered satisfactory. Assuming that all atoms are in general positions, the asymmetric structural unit consists of two lithium and two arsenic atoms.

The crystals had a metallic luster, showed good cleavage parallel to the b axis (needle axis), and were observed to cleave equally well on any of a number of $h0l$ faces, a behavior compatible with the chain structure ultimately found.

The $h0l$ Weissenberg photographs show an unusual pseudo-symmetry. The intensities are nearly identical on either side of the $10\overline{4}$ central row. An orthogonal pseudo-cell can be constructed in which $A = 4a+c$, $B = b$ and $C = c$. A is parallel to the $10\overline{4}$ plane in the monoclinic cell.

The initial set of intensity data was obtained with Mo radiation and a Weissenberg camera. A series of timed photographs of levels normal to b^* for $k = 0$ to 6 was made. The intensities were measured by eye with the aid of calibration spots made by using the crystal itself. A series of timed precession photographs

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* Work done under the auspices of the U.S. Atomic Energy Commission. A preliminary account of this structure was given at the meeting of the American Crystallographic Association at Pasadena, California, U.S.A., June, 1955.

with Zr-filtered Mo radiation was made of the *hk*0 and 0*kl* zones. Lorentz-polarization corrections were applied and all structure factors placed on the same scale by comparing reflections occurring on both Weissenberg and precession films. For the precession data, the *Lp* corrections of Waser (1951) were used. A total of 601 non-zero independent reflections was recorded. No absorption corrections were applied.

The photographic data were adequate for finding the arsenic positions and suggested where the lithium atoms might be. There were, however, several reflections which were unobserved and had been calculated to be moderately strong. In order to remove these apparent discrepancies and to attempt to define the lithium positions as well as possible by X-ray evidence alone, a second set of data was taken with a scintillation counter adapted to the mechanical device described by Evans (1953), again using Mo radiation. Levels for $k = 0$ to 7 were measured out to $\sin\theta/\lambda \simeq 0{\cdot}856$. A crystal with dimensions $0{\cdot}027 \times 0{\cdot}027 \times 0{\cdot}135$ mm. was used. The long axis of the crystal was the rotation axis. Of the 1482 reflections investigated, 1008 were observed greater than zero, 424 were too weak to measure, and 50 occurred at angles too small to be measured accurately. Again, no absorption corrections were made. The small, uniform cross-section of the crystal was favorable for minimizing absorption errors, and the excellent final agreement between observed and calculated structure factors indicates that absorption errors were minor.

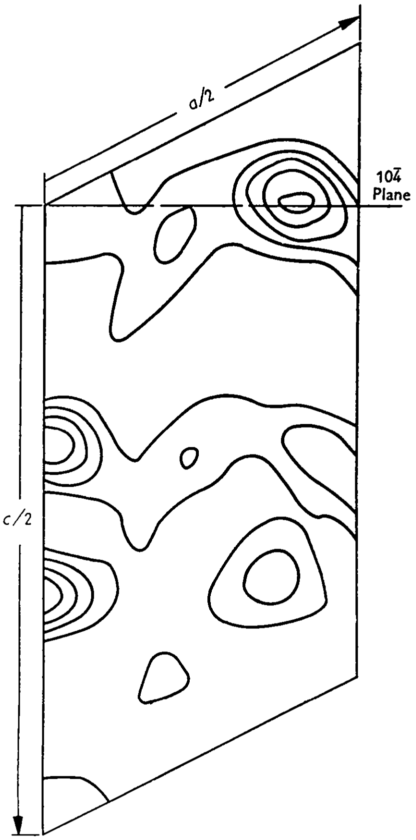

Fig. 1. Patterson projection of LiAs on 010. Contours are at equal arbitrary intervals. The origin peak is not shown.

Determination of the structure

Patterson projections on the 100 and 010 planes were computed. The *h*0*l* Patterson projection is shown in Fig. 1. The pseudo-symmetry of the *h*0*l* layer noted before shows that in projection there are pseudo-mirrors perpendicular to and parallel with the trace of the $10\bar{4}$ plane. The $10\bar{4}$ structure factor is very large so that the arsenic atoms must lie close to the $10\bar{4}$ planes. The *h*0*l* Patterson shows a large peak on $10\bar{4}$ plane through the origin. This peak is produced by the x, z components of the vectors between those atoms lying near $10\bar{4}$ planes. The other main peaks lie along the line $x = 0$ and are produced by vectors normal to the $10\bar{4}$ plane.

The approximate arsenic positions were deduced from the two Patterson projections. Calculated phases from this trial structure were used to compute Fourier projections. No sign changes were indicated. It was, therefore, necessary to use three-dimensional data for further refinement and to locate the lithium atoms.

A three-dimensional Fourier was calculated for the asymmetric portion of the cell with $\Delta x = \Delta y = 0{\cdot}02$ and $\Delta z = 0{\cdot}01$. Phases were those computed with the arsenic atoms only. This Fourier showed several small peaks which might have been the lithium atoms, but only two of these peaks were far enough removed from the arsenic atoms ($> 2{\cdot}5$ Å) to be seriously considered as possible lithium sites. The other peaks were very likely produced by series termination effects and/or experimental errors in the observed structure factors. An $(F_o - F_c)$ Fourier was computed in the region of the two peaks that were thought to be lithium atoms in an attempt to define their positions better. F_c was calculated with the arsenic atoms only. Also, an F_c Fourier was computed in the region of the arsenic atoms in order to correct their positions for series termination effects. The atomic coordinates from these Fourier series are given in Table 1. Structure factors for this model were calculated and gave $R = 14{\cdot}1\,\%$.

Table 1. *Atomic coordinates of* LiAs, *photographic data*

Three-dimensional Fourier	x	y	z
As_1	0·3026	0·9159	0·2993
As_2	0·2847	0·1629	0·1006
Three-dimensional Fourier with series termination correction			
As_1	0·3050	0·9159	0·2995
As_2	0·2890	0·1633	0·1016
Three-dimensional difference Fourier			
Li_1	0·225	0·397	0·328
Li_2	0·208	0·670	0·029

Table 2. *Result of the least-squares refinement of* LiAs *with counter data*

	x	y	z	B
As_1	0·3042 ± 0·0002	0·9143 ± 0·0002	0·2992 ± 0·0001	0·98 ± 0·01
As_2	0·2891 ± 0·0002	0·1626 ± 0·0002	0·1011 ± 0·0001	0·88 ± 0·01
Li_1	0·235 ± 0·005	0·402 ± 0·006	0·329 ± 0·003	2·30 ± 0·37
Li_2	0·232 ± 0·005	0·669 ± 0·005	0·045 ± 0·003	1·92 ± 0·33

With the lithium atoms excluded, $R = 14·7\%$. The scale factor and an isotropic temperature factor ($B = 1·24$ Å^2) were determined from a least-squares solution of the plot of

$$\log (F_o/F_c) = \log (1/K) - B \sin^2 \theta/\lambda^2.$$

Least-squares refinement

With the above structure as a starting point, a least-squares refinement was made with the counter data. Separate scale factor parameters were given to each layer with constant k index, and separate isotropic temperature factor parameters were given to each crystallographically different atom. Only diagonal terms were used. Arsenic form factors were taken from the *Internationale Tabellen* (1935) and the form factors for the neutral lithium atom were those computed by Berghuis *et al.* (1955). All observed reflections were weighted equally. Unobserved reflections were omitted.

The least-squares results are given in Table 2. The agreement of the arsenic parameters with the results, corrected for series termination, in Table 1 is good. Some of the lithium parameters have changed significantly but the general features of the structure have not been altered. One feature that is different, however, is that Li_2 now is farther from the origin. This atom was only 2·83 Å from the one related by the center of symmetry at the origin. This distance is now 2·99 Å, slightly shorter than that found in metallic lithium but not significantly shorter considering the estimated error. It is worth noting, however, that in NaSb (Cromer, 1959), which is isostructural with LiAs, the corresponding distance is quite short.

The observed structure factors and those calculated with the parameters given in Table 2 are listed in Table 3. Omitting the $F_o = 0$, $R = 6·55\%$ with all atoms included and $R = 7·74\%$ with only the arsenic atoms included. It is seen that the lithium atoms have indeed produced a small but definite effect on the measured intensities.

At the higher angles the lithium atoms make a very small contribution to the intensity. The least-squares calculations were repeated using only those structure factors within the Cu $K\alpha$ sphere of reflection. For this calculation R was reduced to 5·57% for all atoms and to 7·14% with only the arsenic atoms. Parameter changes were all less than one standard deviation, but the standard deviations were slightly higher because of the smaller number of observations. Thus, the results obtained by using all data are preferred.

As a final check on the structure, another three-dimensional Fourier series over the asymmetric portion of the cell was computed. The entire set of counter data was used and the phases were those given by the final least-squares cycle. The peak electron den-

Table 3. *Observed and calculated structure factors for* LiAs *from the least-squares refinement of the counter data*

The column headings are $h, k, l, F_{obs.}$ and $F_{calc.}$. If $F_{obs.}$ is negative, the minus sign should be interpreted as 'less than'. If $F_{obs.}$ is zero, the reflection occurred at too small an angle to be measured accurately

h	k	l	$F_{obs.}$	$F_{calc.}$
0	0	2	58	-59
0	0	4	49	-48
0	0	6	39	-36
0	0	8	29	-30
0	0	10	95	95
0	0	12	27	-22
0	0	14	19	-15
0	0	16	16	-11
1	0	-16	32	-33
1	0	-14	43	43
1	0	-12	28	27
1	0	-10	25	-27
1	0	-8	-12	-11
1	0	-6	104	-114
1	0	-4	161	168
1	0	-2	75	66
1	0	0	76	-67
1	0	2	19	-17
1	0	4	123	-127
1	0	6	104	111
1	0	8	30	27
1	0	10	27	-28
1	0	12	9	-8
1	0	14	28	-29
2	0	-16	33	35
2	0	-14	9	-10
2	0	-12	15	14
2	0	-10	85	-89
2	0	-8	30	29
2	0	-6	114	113
2	0	-4	41	-36
2	0	-2	34	27
2	0	0	180	-179
2	0	2	41	39
2	0	4	95	98
2	0	6	24	-25
2	0	8	9	13
2	0	10	60	-58
2	0	12	15	16
2	0	14	31	27
3	0	-18	-11	1
3	0	-16	12	18
3	0	-14	35	-37
3	0	-12	43	-44
3	0	-10	76	82
3	0	-8	-6	-2
3	0	-6	56	48
3	0	-4	114	-113
3	0	-2	60	-79
3	0	0	133	124
3	0	2	14	-8
3	0	4	45	44
3	0	6	64	-61
3	0	8	28	-30
3	0	10	47	47
3	0	12	-11	-2
4	0	-18	-11	-0
4	0	-16	39	-50
4	0	-14	29	30
4	0	-12	9	12
4	0	-10	40	37
4	0	-8	12	-13
4	0	-6	133	-128
4	0	-4	76	72
4	0	-2	18	19
4	0	0	66	59
4	0	2	15	-14
4	0	4	85	-87
4	0	6	42	44
4	0	8	13	7
4	0	10	20	18
5	0	-18	-11	-2
5	0	-16	-10	10
5	0	-14	12	15
5	0	-12	42	40
5	0	-10	95	-92
5	0	-8	-9	0
5	0	-6	27	27
5	0	-4	37	38
5	0	-2	61	54
5	0	0	104	-102
5	0	2	-8	6
5	0	4	16	13
5	0	6	17	18
5	0	8	19	19
5	0	10	38	-38
6	0	-18	-11	-1
6	0	-16	34	42
6	0	-14	33	-32
6	0	-12	35	-34
6	0	-10	17	17
6	0	-8	-8	3
6	0	-6	85	83
6	0	-4	61	-56
6	0	-2	40	-40
6	0	0	21	12
6	0	2	-9	2
6	0	4	49	48
6	0	6	35	-32
6	0	8	18	-15
7	0	-16	26	-32
7	0	-14	-10	5
7	0	-12	16	-18
7	0	-10	62	59
7	0	-8	9	6
7	0	-6	59	-56
7	0	-4	9	4
7	0	-2	19	-19
7	0	0	56	53
7	0	2	-10	0
7	0	4	31	-31
7	0	6	-11	3
8	0	-16	17	-19
8	0	-14	20	20
8	0	-12	34	37
8	0	-10	42	-38
8	0	-8	-10	-3
8	0	-6	32	-29
8	0	-4	27	27
8	0	-2	37	36
8	0	0	33	-31
8	0	2	-11	-2
9	0	-14	14	-11
9	0	-12	-11	-5
9	0	-10	20	-21
9	0	-8	-10	-7
9	0	-6	49	47
9	0	-4	14	-13
9	0	-2	-11	-4
9	0	0	-11	-16
0	0	-10	33	32
0	1	1	0	18
0	1	2	102	-116
0	1	3	45	45
0	1	4	-5	2
0	1	5	102	-115
0	1	6	11	8
0	1	7	39	41
0	1	8	71	72
0	1	9	15	7
0	1	10	-8	-5
0	1	11	10	10
0	1	12	40	-40
0	1	13	14	14
0	1	14	-10	0
0	1	15	31	-32
0	1	16	-11	2
1	1	-17	-11	-6
1	1	-16	17	16
1	1	-15	10	11
1	1	-14	28	29
1	1	-13	15	-7
1	1	-12	39	-38
1	1	-11	49	51
1	1	-10	25	-22
1	1	-9	60	-61
1	1	-8	25	-26
1	1	-7	22	-23
1	1	-6	57	58
1	1	-5	39	38
1	1	-4	93	90
1	1	-3	25	-23
1	1	-2	102	-96
1	1	-1	0	113
1	1	0	34	-36
1	1	1	111	-110
1	1	2	27	-27
1	1	3	17	-16
1	1	4	69	71
1	1	5	31	31
1	1	6	53	54
1	1	7	-7	-6
1	1	8	51	-54
1	1	9	46	49
1	1	10	18	-15
1	1	11	39	-41
1	1	12	13	-11
1	1	13	-10	-3
1	1	14	20	20
1	1	15	-11	8
2	1	-17	-11	-10
2	1	-16	-10	-7
2	1	-15	24	32
2	1	-14	14	-17
2	1	-13	9	-9
2	1	-12	25	-26
2	1	-11	41	-44
2	1	-10	-7	-0
2	1	-9	30	30
2	1	-8	93	96
2	1	-7	41	-40
2	1	-6	24	-22
2	1	-5	102	97
2	1	-4	46	-43
2	1	-3	25	-22
2	1	-2	55	-49
2	1	-1	83	-83
2	1	0	9	8
2	1	1	49	46
2	1	2	111	111
2	1	3	31	-32
2	1	4	28	-29
2	1	5	72	73
2	1	6	31	-33
2	1	7	16	-20
2	1	8	29	-28
2	1	9	32	-32
2	1	10	10	6
2	1	11	14	14
2	1	12	34	35
2	1	13	-10	-10
2	1	14	-11	-9
3	1	-18	-11	-7
3	1	-17	14	15
3	1	-16	12	-14
3	1	-15	27	-32
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3	1	-13	14	13
3	1	-12	50	54
3	1	-11	32	-31
3	1	-10	24	26
3	1	-9	42	41
3	1	-8	25	-23
3	1	-7	52	50
3	1	-6	36	-35
3	1	-5	93	-89
3	1	-4	66	-61
3	1	-3	40	35
3	1	-2	102	100
3	1	-1	50	-45
3	1	0	30	28
3	1	1	54	52
3	1	2	35	-34
3	1	3	39	37
3	1	4	35	-34
3	1	5	58	-59
3	1	6	26	-30
3	1	7	12	14
3	1	8	47	47
3	1	9	14	-19
3	1	10	12	10
3	1	11	20	20
3	1	12	11	-9
3	1	13	-11	9
4	1	-18	13	-23
4	1	-17	-10	2
4	1	-16	12	12
4	1	-15	11	-14
4	1	-14	30	33
4	1	-13	-9	-3
4	1	-12	-8	-1
4	1	-11	62	67
4	1	-10	-7	-8
4	1	-9	52	-48
4	1	-8	73	-74
4	1	-7	14	11
4	1	-6	35	32
4	1	-5	37	-32
4	1	-4	68	65
4	1	-3	10	-7
4	1	-2	16	-13
4	1	-1	93	87
4	1	0	13	-15
4	1	1	58	-56
4	1	2	69	-64
4	1	3	-7	4
4	1	4	28	29
4	1	5	20	-20
4	1	6	37	37
4	1	7	-9	1
4	1	8	-9	-3
4	1	9	31	32
4	1	10	-10	-7
4	1	11	16	-18
5	1	-18	13	20
5	1	-17	14	-19
5	1	-16	-10	8
5	1	-15	34	38
5	1	-14	10	9
5	1	-13	12	-8
5	1	-12	43	-45
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5	1	-8	57	53
5	1	-7	52	-48
5	1	-6	8	10
5	1	-5	83	80
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5	1	-3	21	-19
5	1	-2	67	-62
5	1	-1	9	-10
5	1	0	16	-18
5	1	1	-8	-6
5	1	2	45	50
5	1	3	28	-32
5	1	4	8	9
5	1	5	39	46
5	1	6	-8	5
5	1	7	-9	-8
5	1	8	25	-27
5	1	9	-9	-3
6	1	-18	-11	12
6	1	-17	-10	11
6	1	-16	-10	-12
6	1	-15	-10	-8
6	1	-14	32	-36
6	1	-13	13	9
6	1	-12	21	21
6	1	-11	50	-47
6	1	-10	16	16
6	1	-9	37	35
6	1	-8	28	29
6	1	-7	19	18
6	1	-6	26	-25
6	1	-5	19	-17
6	1	-4	56	-53
6	1	-3	19	15
6	1	-2	35	34
6	1	-1	55	-53
6	1	0	18	17
6	1	1	34	34
6	1	2	20	20
6	1	3	19	13
6	1	4	18	-18
6	1	5	-10	-9
6	1	6	-10	-26
6	1	7	-11	9
7	1	-17	11	12
7	1	-16	-10	-2
7	1	-15	23	-26
7	1	-14	-10	10
7	1	-13	-9	-2
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7	1	-11	31	29
7	1	-10	17	12
7	1	-9	16	-13
7	1	-8	51	-50
7	1	-7	30	24
7	1	-6	-8	2
7	1	-5	46	-42
7	1	-4	17	14
7	1	-3	-9	1
7	1	-2	28	24
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8	1	-9	17	-15
8	1	-8	-7	4
8	1	-7	26	-26
8	1	-6	12	14
8	1	-5	31	29
8	1	-4	29	28
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8	1	-2	29	-28
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8	1	0	18	-15
8	1	1	14	-13
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9	1	-13	-11	8
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9	1	-10	-10	-1
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9	1	-8	29	30
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9	1	-5	10	12
9	1	-4	21	-22
9	1	-3	-10	6
9	1	-2	-11	-3
9	1	-1	26	-26
0	2	0	0	0
0	2	1	0	35
0	2	2	49	-54
0	2	3	114	-129
0	2	4	43	43
0	2	5	7	-3
0	2	6	37	36
0	2	7	76	87
0	2	8	52	-30
0	2	9	17	-19
0	2	10	-8	1
0	2	11	-8	9
0	2	12	16	-16
0	2	13	41	-40
0	2	14	-10	15
0	2	15	-11	4
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3	5	-8	14	10
3	5	-7	11	-7
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6	7	-5	-11	9
6	7	-4	-11	-5
6	7	-3	26	-26

sities for As_1 and As_2 were 185 and 192 e.Å^{-3} and for Li_1 and Li_2, 7·6 and 6·6 e.Å^{-3}. There were also peaks of height 7·1 and 5·5 e.Å^{-3}, but these were too close to the arsenic atoms to be considered as lithium atoms and were presumably caused by experimental errors and/or series termination effects. Finally, a complete (F_o-F_c) Fourier was computed where F_c was calculated with arsenic atoms only. The two largest peaks of 6·6 and 7·1 e.Å^{-3} were at positions close to those of Li_1 and Li_2 determined from the least-squares refinement. It is of interest to note that the peak heights from the difference Fourier are in the order indicated by the temperature factors from the least-squares refinement, whereas in the Fourier the order was reversed. Near As_1 positive peaks of 4·6 and 4·3 and negative peaks of 4·7 and 4·3 e.Å^{-3} appeared. These peaks indicate a small anisotropy of thermal motion but no attempt was made to account for this in the calculations. The arsenic peaks in the Fourier were very nearly spherical. All of the spurious peaks of the Fourier disappeared in the difference Fourier and, except as noted above, the electron density everywhere was within ±2·8 e.Å^{-3}.

The peak positions from these Fouriers are given in Table 4. They were determined by the 27 point least-squares Gaussian interpolation method of Shoemaker *et al.* (1950). Fig. 2 is a composite of sections

Table 4. *Atomic coordinates of* LiAs *obtained from Fourier with the counter data*

	x	*y*	*z*
Three-dimensional Fourier			
As_1	0·3043	0·9147	0·2996
As_2	0·2892	0·1634	0·1010
Li_1	0·219	0·411	0·331
Li_2	0·211	0·667	0·043
Three-dimensional difference Fourier			
Li_1	0·232	0·406	0·328
Li_2	0·228	0·670	0·042

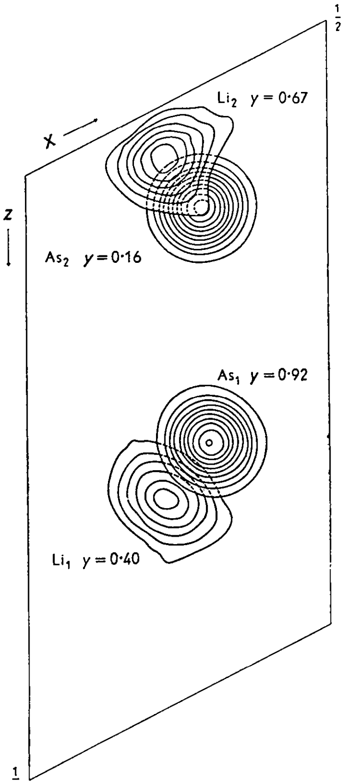

Fig. 2. Composite of electron-density sections near the atoms. The arsenic sections are from the three-dimensional Fourier with contour intervals at 20·0 e.Å^{-3}. The lithium sections are from the three-dimensional (F_o-F_c) Fourier with contour intervals at 1·0 e.Å^{-3}. The outermost contour is zero for the arsenic atoms and 1·0 for the lithium atoms.

near the atoms taken from the final Fourier and the difference Fourier.

Accuracy of the structure

The standard deviations of the parameters were computed from the expression

$$\sigma(\xi_i) \simeq \left[\frac{\Sigma(\Delta F)^2}{(m-s)\Sigma\left(\dfrac{\partial F}{\partial \xi_i}\right)^2}\right]^{\frac{1}{2}}$$

where m is the number of observations, s is the number of variables and ΔF has its usual significance. This approximation must be used whenever the full matrix of the least-squares normal equations has not been computed. The $\sigma(x_i)$ and $\sigma(z_i)$ were about 25% smaller than the $\sigma(y_i)$. This difference results from two causes. First, because data were taken about the b axis only, the index k does not have values > 7. The $\Sigma(\partial F/\partial y_i)^2$ are therefore smaller than the corresponding x and z terms. Second, for a monoclinic cell, the above approximation underestimates the x and z standard deviations. For the $h0l$ projection of NaSb (Cromer, 1959), a compound isostructural with LiAs, the diagonal approximation underestimated the standard deviations by 12 to 22%. The x and z standard deviations given in Table 2 are accordingly 1·25 times that given by the above formula. This correction essentially equalizes the error in the three crystallographic directions. The standard deviation of position for the arsenic atoms is thus 0·0023 Å and for the lithium atoms 0·052 Å. The standard deviations of As–As, Li–As, and Li–Li distances are therefore 0·003, 0·052, and 0·074 Å, respectively.

Discussion of the structure

A projection of the unit-cell contents on 010 is shown in Fig. 3. The y coordinate is given beside each atom. The various interatomic distances, calculated from the parameters given in Table 2, are shown in Table 5.

Table 5. *Interatomic distances in* LiAs

The standard deviation for As–As distances is 0·0033 Å, for Li–As distances 0·052 Å and for Li–Li distances, 0·074 Å

	d		d
As$_1$–As$_2$(+)	2·454 Å	Li$_1$–Li$_3$	3·00 Å
–As$_3$	2·472	–Li$_7$	3·78
Li$_1$–As$_1$	2·75	–Li$_7$(+)	3·22
–As$_1$(−)	2·63	–Li$_6$	3·74
–As$_3$	2·85	–Li$_5$	3·59
–As$_5$	2·77	–Li$_5$(−)	3·59
–As$_7$	2·80	–Li$_2$	3·34
–As$_2$	2·89	–Li$_9$	3·67
Li$_2$–As$_2$	2·71	Li$_2$–Li$_5$	3·74
–As$_2$(+)	2·64	–Li$_9$	2·99
–As$_9$	2·83	–Li$_{10}$	3·78
–As$_4$	2·77	–Li$_{10}$(+)	3·22
–As$_{10}$	2·88	–Li$_4$	3·00
–As$_1$	2·86	–Li$_{12}$	3·67

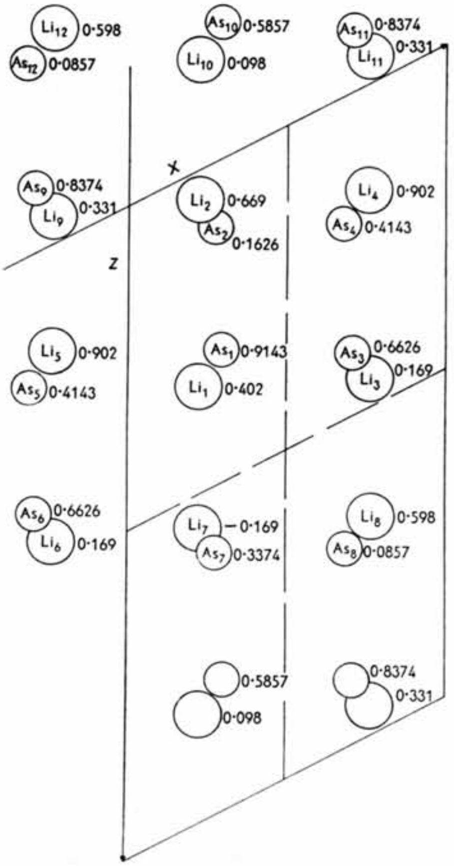

Fig. 3. Projection of the structure on 010. The y coordinate is given beside each atom.

The nomenclature used in Table 5 refers to Fig. 3. A (+) or (−) following an atom means that the atom referred to is one cell above, or below the one shown in Fig. 3. Fig. 4 is a drawing illustrating packing of the unit-cell contents.

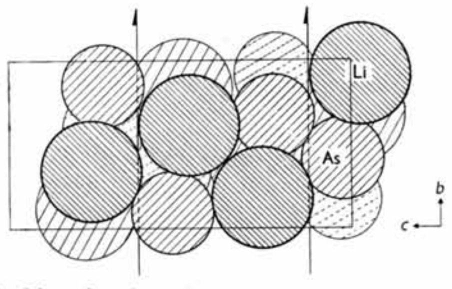

Fig. 4. Packing drawing of the unit-cell contents of LiAs. The view is normal to the 100 plane.

The arsenic atoms are arranged in infinite spiral chains parallel to the b axis. There are two such chains spiralling in opposite directions passing through the unit cell. The As–As bonds are alternately 2·454 and 2·472 Å, a difference of 0·018 Å, and the angles are alternately 105° 9′ and 108° 28′. The standard deviation of these bonds is 0·0033 Å. According to Cruickshank (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 nonbonded 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.

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The Crystal Structure of NaSb*

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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 $a = 6·80 \pm 0·02$, $b = 6·34 \pm 0·02$, $c = 12·48 \pm 0·04$ Å, and $\beta = 117·6 \pm 0·2°$. 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

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