The Crystal Structure of SiAs

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The crystal structure of the phase SiAs has been determined on the basis of single-crystal Weissenberg data. The structure is monoclinic of space group $C2/m$. The unit cell contains twelve formula units SiAs and the dimensions obtained from a Guinier powder pattern are

$$a = 15.98 \text{ Å}, \quad b = 3.668 \text{ Å}, \quad c = 9.529 \text{ Å}, \quad \beta = 106.0°.$$

The structure may be described as being built up of layers of distorted As octahedra sharing edges. Each octahedron is filled with two Si atoms. The normal tetrahedral arrangement of the silicon atoms is fulfilled with three arsenic and one silicon atom as nearest neighbours. All arsenic atoms have three silicon atoms as closest neighbours and the coordination is pyramidal.

In 1941 Klemm and Pirscher [1] reported on an investigation of the silicon-arsenic system. They gave the phase diagram and found that two intermediate phases exist with the compositions SiAs and $SiAs_2$, and described various properties of these compounds. They also gave the X-ray powder patterns of the two phases. The crystal structures of these and also of some related compounds are being studied at this Institute. The present article will report on the structure determination of SiAs.

EXPERIMENTAL

Crystals of SiAs were prepared by melting the finely powdered elements together. The synthesis was carried out in an evacuated sealed silica tube with a very slight excess of arsenic. At about 1100°C the reaction was found to reach completion in 2 h. Slow cooling to room temperature gave a sample consisting of small balls with shiny metallic appearance. A careful study under the microscope showed that tiny needles had grown perpendicular to the surface of the balls and also on the wall of the tube.

Crystals, picked out from the crushed balls, were shaped as plates with a grey metallic surface. Guinier powder patterns proved the needles to consist of the same phase as the plates.

A needle of about 0.5 mm in length was cut to pieces. One of these with the dimensions $0.1 \times 0.005 \times 0.005$ mm was mounted along the needle axis and was used to collect X-ray data with the Weissenberg technique. The $h0l$, $h1l$ and $h2l$ reflections were recorded with nickel filtered copper radiation. The intensities were measured by means of a calibrated film strip. The absorption correction was negligible and was not applied.

Table 1. Crystallographic data for SiAs. Symmetry: monoclinic

Unit cell dimensions	a	15.979 ± 0.004 Å
	b	3.668 ± 0.001 Å
	c	9.529 ± 0.002 Å
	β	$106.00 \pm 0.01°$
Unit cell volume	537 Å³	
Unit cell content	12 formula units	
Density obs.	$(g \cdot cm^{-3})$	3.76_0[1]
Density calc.	$(g \cdot cm^{-3})$	3.82_1

Table 2. Guinier powder pattern of SiAs, $CuK\alpha_1$ radiation. Internally calibrated with KCl ($a = 6.2930$ Å).

Intensity	$\sin^2\Theta$ (obs.) 10^{-6}	hkl	$\sin^2\Theta$ (calc.) 10^{-6}
w	2 175	201	2 178
vw	2 827	002	2 829
vw	2 909	20$\bar{2}$	2 905
vw	3 802	40$\bar{1}$	3 801
vw	4 022	400	4 023
w+	4 763	202	4 765
w	4 992	40$\bar{2}$	4 992
m	5 658	401	5 661
m	6 363	003	6 365
st	6 675	$\begin{cases} 310 \\ 31\bar{1} \end{cases}$	$\begin{cases} 6\ 674 \\ 6\ 684 \end{cases}$
m	7 026	11$\bar{2}$	7 026
m	8 084	$\begin{cases} 311 \\ 31\bar{2} \end{cases}$	$\begin{cases} 8\ 079 \\ 8\ 107 \end{cases}$
m	8 766	203	8 766
vw	9 055	$\begin{cases} 600 \\ 60\bar{2} \end{cases}$	$\begin{cases} 9\ 053 \\ 9\ 091 \end{cases}$
vw	10 324	11$\bar{3}$	10 329
w	10 949	31$\bar{3}$	10 946
vw	11 205	$\begin{cases} 51\bar{2} \\ 60\bar{3} \end{cases}$	$\begin{cases} 11\ 201 \\ 11\ 232 \end{cases}$
w	11 723	113	11 725
vw	12 570	511	12 567
vw	13 578	51$\bar{3}$	13 574
w	14 171	204	14 181
vw	14 686	602	14 672
vst	15 131	313	15 131
vw	15 838	$\begin{cases} 71\bar{1} \\ 512 \end{cases}$	$\begin{cases} 15\ 812 \\ 15\ 851 \end{cases}$
vw	16 325	$\begin{cases} 71\bar{2} \\ 20\bar{5} \end{cases}$	$\begin{cases} 16\ 306 \\ 16\ 361 \end{cases}$
w	16 744	710	16 732
vw	16 917	$\begin{cases} 80\bar{3} \\ 114 \end{cases}$	$\begin{cases} 16\ 878 \\ 16\ 907 \end{cases}$
vw	17 072	40$\bar{5}$	17 053

DETERMINATION OF THE STRUCTURE

The crystallographic data of SiAs and the Guinier powder pattern are given in Tables 1 and 2.

All reflections hkl with $h + k \neq 2n$ are absent. The possible space groups are thus $C2$, Cm, and $C2/m$. The close similarity of the intensity distribution of the $h0l$ and $h2l$ layer lines indicates, however, that $C2/m$ is the actual symmetry of the structure.

The Patterson projection was calculated from the $h0l$ data. The positions of the As atoms could be easily found from this map. The Si atoms showed up after a few successive Fourier calculations of the electron density projection. The structure thus obtained was in good agreement with the Patterson projection.

Assuming the symmetry to be $C2/m$ all the atoms had to be situated in the mirror planes, $i.e.$ to have the y parameters 0 or $\frac{1}{2}$. The distribution of the atoms could thus be found from spatial considerations, giving the following preliminary structure

			x	y	z
As$_1$	in	4 (i)	0.164	0.5	0.174
As$_2$	»	»	0.461	0.5	0.176
As$_3$	»	»	0.349	0	0.453
Si$_1$	»	»	0.253	0	0.203
Si$_2$	»	»	0.367	0	0.086
Si$_3$	»	»	0.430	0.5	0.414

This arrangement of the atoms was confirmed by the appearance of the Patterson projection calculated on the basis of the $0kl$ reflections obtained from a Weissenberg photograph of one of the plate-like crystals. (This photograph was considerably affected by absorption and was not used elsewhere in the structure determination.)

The refinement of the structure was carried out by least-squares techniques using a program written by Åsbrink and Bränden.[2] The calculation was based on all observed $h0l$, $h1l$, and $h2l$ independent reflections. The atomic parameters and temperature factors are found in Table 3. The reliability index after eight cycles was 0.082. The observed and calculated structure factors for the layer lines $h0l$ and $h1l$ are given in Table 4.

Table 3. Fractional atomic parameters. Space group $C2/m$ (0, 0, 0; $\frac{1}{2}$, $\frac{1}{2}$, 0) $+$

Atom	Point Position	x	y	z	B	σ
As$_1$	4 (i)	0.1632 $\pm$ 0.0003	0.5	0.1738 $\pm$ 0.0005	1.42	0.08
As$_2$	4 (i)	0.4631 $\pm$ 0.0003	0.5	0.1761 $\pm$ 0.0005	1.54	0.09
As$_3$	4 (i)	0.3479 $\pm$ 0.0003	0	0.4543 $\pm$ 0.0005	1.37	0.09
Si$_1$	4 (i)	0.2613 $\pm$ 0.0008	0	0.2076 $\pm$ 0.0012	1.33	0.20
Si$_2$	4 (i)	0.3697 $\pm$ 0.0007	0	0.0838 $\pm$ 0.0012	1.30	0.21
Si$_3$	4 (i)	0.4339 $+$ 0.0008	0.5	0.4116 $\pm$ 0.0013	1.37	0.21

Table 4. Comparison between observed and calculated structure factors.

h	k	l	F_o	F_c	h	k	l	F_o	F_c
0	0	2	27	− 34	8	0	$\bar{5}$	150	−132
0	0	3	292	−294	8	0	$\bar{7}$	115	−107
0	0	4	40	− $\bar{4}$2	10	0	8	69	63
0	0	5	124	135	10	0	$\bar{5}$	110	−105
0	0	6	54	68	10	0	3	97	100
0	0	8	156	− 149	10	0	2	137	132
0	0	11	76	84	10	0	1	118	126
2	0	8	57	− 58	10	0	0	239	−213
2	0	6	40	− 49	10	0	$\bar{1}$	90	− 87
2	0	5	137	142	10	0	$\bar{3}$	218	190
2	0	4	81	− 83	10	0	$\bar{4}$	78	66
2	0	3	139	145	10	0	$\bar{6}$	105	− 94
2	0	2	82	− 92	10	0	$\bar{7}$	100	− 99
2	0	1	43	52	12	0	3	91	− 82
2	0	$\bar{1}$	26	− 24	12	0	2	57	56
2	0	$\bar{2}$	71	77	12	0	$\bar{2}$	59	− 64
2	0	$\bar{3}$	148	−135	12	0	$\bar{5}$	132	127
2	0	$\bar{5}$	97	−109	12	0	$\bar{8}$	56	− 59
2	0	$\bar{6}$	83	81	14	0	6	81	− 71
2	0	$\bar{8}$	63	64	14	0	1	111	−101
4	0	9	70	− 65	14	0	$\bar{2}$	156	159
4	0	8	109	112	14	0	$\bar{5}$	136	−116
4	0	6	104	102	14	0	$\bar{8}$	82	71
4	0	5	54	− 59	16	0	$\bar{3}$	111	101
4	0	4	84	− 87	16	0	0	74	− 65
4	0	1	178	195	16	0	$\bar{3}$	56	50
4	0	0	78	− 88	16	0	$\bar{6}$	41	− 53
4	0	$\bar{1}$	82	− 89	1	1	11	35	− 48
4	0	$\bar{2}$	244	−256	1	1	9	49	− 58
4	0	$\bar{3}$	56	52	1	1	8	104	103
4	0	$\bar{4}$	129	120	1	1	6	73	75
4	0	$\bar{5}$	174	204	1	1	5	58	− 58
4	0	$\bar{7}$	71	− 75	1	1	4	62	− 60
4	0	$\bar{8}$	77	− 83	1	1	3	64	− 57
4	0	$\overline{10}$	73	86	1	1	1	45	49
6	0	10	58	− 51	1	1	$\bar{2}$	122	−154
6	0	7	64	64	1	1	$\bar{3}$	60	58
6	0	6	134	130	1	1	$\bar{5}$	197	208
6	0	5	93	− 87	1	1	$\bar{8}$	90	−103
6	0	3	195	−182	1	1	$\overline{10}$	32	53
6	0	2	82	82	3	1	9	47	− 61
6	0	1	80	81	3	1	8	51	− 65
6	0	0	140	136	3	1	6	129	124
6	0	$\bar{1}$	90	− 95	3	1	4	130	−124
6	0	$\bar{2}$	46	− 43	3	1	3	215	−244
6	0	$\bar{3}$	64	− 58	3	1	2	21	25
6	0	$\bar{4}$	108	101	3	1	1	111	104
6	0	$\bar{5}$	109	103	*3	1	0	236	341
6	0	$\bar{8}$	109	−148	3	1	$\bar{1}$	97	− 96
6	0	$\overline{11}$	86	84	3	1	$\bar{2}$	43	− 43
8	0	9	61	50	3	1	$\bar{3}$	185	−178
8	0	6	90	− 85	3	1	$\bar{4}$	72	78
8	0	3	79	74	3	1	$\bar{5}$	130	129
8	0	$\bar{2}$	70	64	3	1	$\bar{8}$	156	−164
8	0	$\bar{3}$	65	− 56	3	1	$\overline{11}$	74	79
8	0	$\bar{4}$	104	83	5	1	6	63	− 72

h	k	l	F_o	F_c		h	k	l	F_o	F_c
5	1	5	43	47		9	1	$\bar{2}$	58	− 52
5	1	$\bar{4}$	31	− 46		9	1	$\bar{5}$	105	105
5	1	3	129	136		9	1	$\bar{8}$	97	− 97
5	1	2	60	− 58		9	1	$\bar{1}\bar{1}$	49	57
5	1	1	62	58		11	1	6	87	− 77
5	1	$\bar{2}$	72	− 79		11	1	2	100	91
5	1	$\bar{3}$	125	−131		11	1	$\bar{3}$	43	39
5	1	$\bar{4}$	36	43		11	1	$\bar{4}$	69	61
5	1	$\bar{5}$	134	−128		11	1	$\bar{5}$	123	−116
5	1	$\bar{6}$	71	79		11	1	$\bar{7}$	74	− 71
7	1	9	47	− 47		11	1	$\bar{8}$	88	77
7	1	8	76	81		13	1	6	67	− 63
7	1	6	74	76		13	1	5	57	− 58
7	1	5	89	− 90		13	1	3	123	120
7	1	4	68	− 72		13	1	2	90	79
7	1	1	239	205		13	1	0	156	−136
7	1	0	211	−175		13	1	$\bar{3}$	136	127
7	1	$\bar{1}$	130	−108		13	1	$\bar{5}$	37	− 42
7	1	$\bar{2}$	249	−231		13	1	$\bar{6}$	90	− 77
7	1	$\bar{3}$	128	130		13	1	$\bar{7}$	51	− 51
7	1	$\bar{4}$	138	140		13	1	$\bar{8}$	89	84
7	1	$\bar{5}$	92	84		15	1	$\bar{2}$	63	− 42
7	1	$\bar{6}$	74	70		15	1	$\bar{4}$	36	− 31
7	1	$\bar{7}$	123	−115		15	1	$\bar{5}$	87	84
7	1	$\bar{9}$	51	74		15	1	$\bar{6}$	44	− 46
7	1	$\bar{10}$	80	84		17	1	3	36	34
9	1	8	25	33		17	1	1	117	−107
9	1	$\bar{6}$	71	68		17	1	$\bar{2}$	165	150
9	1	5	97	− 94		17	1	$\bar{5}$	87	− 84
9	1	3	121	−113		17	1	$\bar{7}$	74	70
9	1	2	87	80		17	1	$\bar{8}$	31	26
9	1	0	30	31		19	1	0	26	− 30
9	1	$\bar{1}$	41	− 37		19	1	$\bar{5}$	49	− 48

* Reflection not used in the least-square refinement.

DESCRIPTION OF THE STRUCTURE

The structure of SiAs thus derived is analogous to the one found by Bryden [3] for GaTe and GeAs (private communication) and described in a recent article by Pearson.[4] The atomic arrangement can be visualized as being built up of layers (Fig. 1) consisting of distorted As-octahedra joined by sharing edges (Fig. 2).

Each octahedron contains two silicon atoms. The environment of each of the latter is the normal one for a group IV element, i.e. tetrahedral comprising the silicon neighbour and three arsenic atoms. This is also in agreement with a suggestion by Hulliger and Mooser [5] which was put forward on the basis of a discussion of the electrical properties of compounds of this type. In Fig. 3 the bond lengths and angles are given for the two different types of octahedra which form the structure. The most obvious difference between the two kinds of polyhedra is in the orientation of the pairs of silicon atoms.
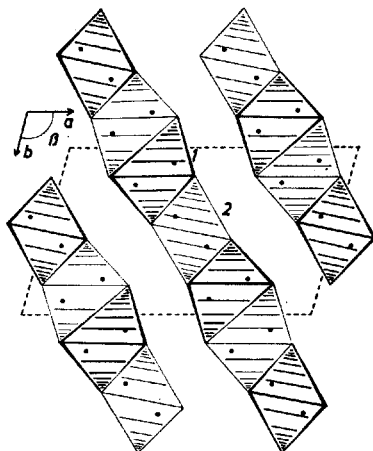
Fig. 1. Projection of structure on (010). Dots are silicon atoms and all corners represent arsenic atoms. 1 and 2, found in all figures, points out the two different types of polyhedra.
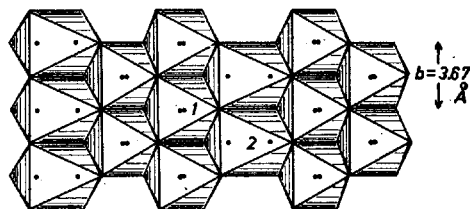

Fig. 2. The octahedra arrangement in one layer. Dots are silicon atoms. Projection perpendicular to the layer.
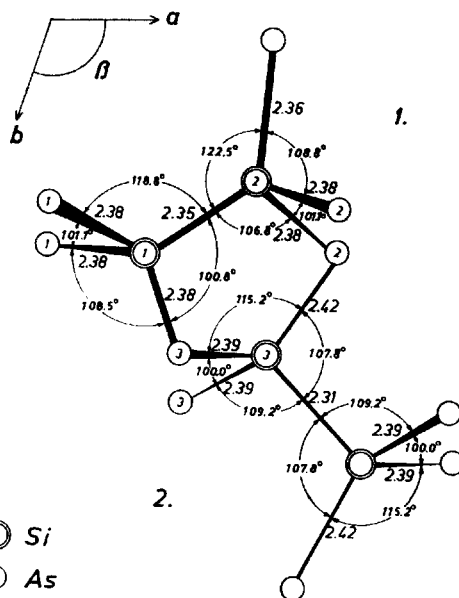

Fig. 3. Bond distances and angles. Small numbers refer to Table 3. Arsenic atoms are a bit twisted to show the coordination.

All the arsenic atoms have three close neighbours arranged to form a pyramid. The distances between the arsenic atoms (representing the peak of the pyramid) and the silicon atoms which form the approximately equilateral base, range from 2.36 to 2.42 Å. The distances to the more remote arsenic and silicon neighbours of a particular arsenic atom are all above 3.5 Å. Between

arsenic atoms of adjacent layers the shortest distance is 3.60 Å. The geo-metrical environment of the arsenic atoms in SiAs is thus very similar to the one present in the metallic form of elementary arsenic.

The structure of SiAs also shows some resemblance to the new dense forms of silicon and germanium recently studied by Kasper and Richards.[6] These compounds are built up of tetrahedra which are distorted in such a way that the arrangement may alternatively be looked upon as being formed by octa-hedra with two further atoms within them.

Further structural studies on compounds between Group IV and V elements are in progress.

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