Chemica Scripta. 1975, 8, 63–69

Preparative and Crystal Structure Studies on Orthorhombic Silicon Monophosphide

Tommy Wadsten

Department of Inorganic Chemistry, Arrhenius Laboratory, University of Stockholm, Stockholm, Sweden

Received November 5, 1974

Abstract

Preparative and crystal structure studies on orthorhombic silicon monophosphide. Wadsten, T. (Department of Inorganic Chemistry, Arrhenius Laboratory, University of Stockholm, Fack, S-104 05 Stockholm, Sweden). *Chemica Scripta* (*Sweden*) 1975, 8 (2), 63–69.

Orthorhombic silicon monophosphide has been prepared as very thin crystal flakes by transport reactions and as prismatic crystals by deposition from molten tin. The material has been studied by electron microscopy and by electron and X-ray diffraction techniques. The crystal structure of $Cmc2_1$ symmetry has been determined and refined to a final R value of 0.036. The unit cell has the dimensions $a=3.5118\pm4$ Å, $b=20.488\pm2$ Å, and $c=13.607\pm4$ Å and contains 24 units of SiP. The structure is built up of layers which may be formally described as composed of P_6 octahedra joined by edges. The octahedron contains two Si atoms, each of which has a rather regular tetrahedral environment of one Si and three P atoms. The P atoms have an one-sided environment of three closely approaching Si atoms. The P–P contacts between adjacent layers are rather long. The coordination and interatomic distances are compared with those in other compounds of silicon and phosphorus. The structure is also compared with the related monoclinic layer structure of SiAs type.

Introduction

The existence of silicon monophosphide was first reported by Biltz et al. [1], who prepared the substance by reacting elementary silicon and phosphorus in a sealed system. The yellowish brown reaction product was found to have the composition SiP. Its X-ray powder pattern was represented in the article by a "Strichdiagram". Several scientists have subsequently contributed to the knowledge of this compound. Fritz and Berkenhoff [2] obtained a mixture of silicon monophosphide and silicon by thermal decomposition of an amorphous blue–black product, Si_2P, which they prepared by reacting SiH_4 and PH_3. They registered the I.R. spectrum of the mixture of SiP and Si and found it to be very similar to the spectrum obtained for a SiP sample prepared according to Biltz et al. [1].

Stickler et al. in a series of papers [3–5] described the results of investigations of precipitations obtained by diffusion of phosphorus into silicon crystals. They found the precipitate to consist of SiP, by comparison with silicon monophosphide samples obtained from the elements by a transport reaction with iodine. The precipitate was characterized by means of electron diffraction techniques, while X-ray powder patterns and poor single-crystal photographs could be obtained for the extremely thin crystalline samples obtained in the transport experiments.

A different technique for preparing silicon phosphide was introduced by Spring Thorpe [6] who obtained such crystals from a solution of silicon and phosphorus in an excess of molten tin which, after the crystallization was removed by hot, concentrated hydrochloric acid. The formula of the crystals was, however, reported to be SiP_2.

Osugi, Namikawa and Tanaka [7] prepared a series of silicon phosphides by reacting the elements at high pressures.

The results reported by the investigators quoted above show considerable divergences. It is possible, nevertheless, by a comparison of the X-ray and electron diffraction data reported, to draw definite conclusions concerning the identity of the various preparations. Thus it is obvious that all the experiments performed at not-too-high pressures have given the same modification of silicon monophosphide. The further phase obtained by Osugi et al. [7] at higher pressures may be polymorphos of silicon monophosphide or, may possess other stoichiometries. One of these substances has actually been reported to possess a sphalerite (ZnS cubic) type of structure, indicating the formula SiP, while another of the products was identified as SiP_2 of pyrite type, previously reported by the present author [8] and by Donohue et al. [9].

The interpretations of the diffraction data given by the various investigators show very marked divergences among themselves. As there is no doubt about the identity of their materials, this must be due, in most cases to the very limited number of data, obtained under rather special conditions. Some authors have tried to interpret their data assuming silicon monophosphide to be isomorphous with silicon monoarsenide [10, 11]. This assumption has turned out to be in error (cf. below).

The work which will be described in this article has been concerned with studies on the preparation and crystal structure of silicon monophosphide. Further work on the thermal decomposition of this and related compounds will be described in a future publication in this journal.

Preparation

In this investigation silicon monophosphide has been prepared by heating of the elements in a sealed system, by transport reaction techniques, and by crystallization from molten tin. The starting materials were fine-grained silicon (Kock-Light 99.99%) and red phosphorus (Grave 99.5%). The iodine used in the transport reactions was Merck resublimed, and the tin for the solution synthesis was Baker Analyzed, 99.9%.

In order to find suitable conditions for reacting silicon and red phosphorus a DTA technique was used. A small amount (20–30 mg) of a mixture of the reactants was sealed in an evacuated silica tube (outer diameter 3 mm, inner diameter 1.5 mm and length 30 mm). Both sample and reference holders were gently inserted into tightly fitting platinum tubes, covering the junctions of the differential thermocouple. This set-up assures good contacts for thermocouple and allows convenient exchange of specimen holders. As reference material the termally inactive substance kaoline was used. For the temperature calibration the

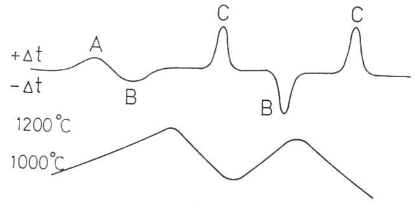

Fig. 1. Schematic representation of a DTA curve showing formation and decomposition of SiP (*upper curve*) and temperature program (*lower curve*).

reversible phase transition, at 925°C, of strontium carbonate was used as recommended by the International Confederation for Thermal Analysis which also provided the test sample.

The information obtained from the differential thermal analysis experiments, which were performed with a heating rate of 10°/min, is collected in Fig. 1. Peak A represents the sluggish thermal effect associated with the formation of SiP. Peak B corresponds to the decomposition of the compound by a process which is not completely known. In order that this peak should be well resolved from peak A the temperature had to be somewhat lowered from the reaction temperature before it was increased to the decomposition point. SiP is again formed after the temperature has been slightly increased and then lowered as indicated in the figure. The formation process is associated with the strongly exothermic peak C.

It was found advantageous from the point of view of crystal growth to prepare SiP at a reaction temperature corresponding to C in the DTA experiments. Thus, the mixture of silicon and red phosphorus to be reacted (up to 0.5 g) was heated in a sealed, evacuated silica tube (8 and 6 mm outer and inner diameter respectively), and length 150 mm, to a temperature well above C, viz. 1 100°C. The temperature was then slowly decreased (10°/hour) by several hundred degrees.

Table I. *Guinier powder pattern of SiP, CuKα_1 radiation. Internally calibrated with KCl ($a = 6.2930$ Å)*

I_{obs}	$h\ k\ l$	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	d_{obs} (Å)	d_{calc} (Å)
12	0 2 1	0.00883	0.00886	8.197	8.184
40	0 0 2	0.01281	0.01282	6.806	6.804
20	0 4 0	0.02262	0.02262	5.121	5.122
25	0 0 4	0.05127	0.05127	3.402	3.402
3	0 6 1	0.05409	0.05409	3.312	3.312
80	1 3 1	0.06402	0.06403	3.044	3.044
55	1 3 2	0.07359	0.07365	2.839	2.838
19	1 5 0	0.08350	0.08344	2.666	2.666
19	1 5 1	0.08671	0.08665	2.616	2.617
30	0 8 0	0.09050	0.09046	2.560	2.561
17	0 8 1	0.09365	0.09366	2.517	2.517
12	1 5 2	0.09613	0.09626	2.484	2.483
8	0 8 2	0.10315	0.10328	2.398	2.397
1	1 5 4	0.13483	0.13471	2.098	2.099
1	0 10 1	0.14469	0.14455	2.025	2.026
1	1 7 3	0.14636	0.14620	2.013	2.014
2	0 10 2	0.15430	0.15416	1.961	1.962
6	1 9 1	0.16559	0.16579	1.893	1.892
1	1 7 4	0.16854	0.16863	1.876	1.876
3	1 9 2	0.17550	0.17541	1.839	1.839
100	2 0 0	0.19240	0.19243	1.756	1.756
1	1 7 5	0.19775	0.19747	1.732	1.733
12	2 0 2	0.20521	0.20525	1.700	1.700
7	1 1 7 0 12 1	0.20652	0.20653 0.20674	1.695	1.695 1.694
28	1 9 4	0.21374	0.21386	1.666	1.666
4	2 2 3	0.22684	0.22692	1.617	1.617
17	2 0 4	0.24363	0.24369	1.561	1.560
19	2 6 2	0.25610	0.25613	1.522	1.522
2	0 14 0	0.27713	0.27703	1.463	1.463
17	2 8 0	0.28302	0.28289	1.448	1.448
12	2 8 1	0.28622	0.28609	1.439	1.440
13	2 8 2	0.29574	0.29570	1.416	1.416
3	1 13 4	0.33796	0.33824	1.325	1.324
3	0 16 0	0.36187	0.36183	1.280	1.281

The product thus obtained consisted of extremely thin crystalline flakes, up to 1 mm in width. It was found that a low rate of decreasing the temperature favoured the formation of large crystals. The X-ray powder pattern of the substance is given in Table I. The very thin crystals gave rather poor single-crystal X-ray photographs. On the other hand, they gave excellent electron diffraction spot patterns (cf. below). Fig. 2 reproduces a transmission electron microscope photograph of a SiP crystal prepared in this way. The photographs show staircase shaped areas of uniform blackening which are likely to reflect the layer-like structure of the compound (cf. below). The infrared spectrum registered for a SiP sample prepared in this way is illustrated in Fig. 3, which also shows the corresponding curve obtained by Fritz and Berkenhoff [2]. The agreement is very satisfactory.

Addition of iodine as a transport agent was found to highly favour the formation of large SiP crystals. The experiments were performed in silica tubes (inner diameter 6 mm and length 200 mm) with up to 0.25 g of each of the reactants and 5–10 mg of iodine. The temperature of the hot end of the tube was kept at 1 100°C while the cold end temperature was several hundred degrees lower. After a few days large crystals of SiP were obtained but they were all very thin; in the μm region. In some experiments crystal flakes measuring up to several cm were formed. The X-ray and electron diffraction patterns given by such crystals were similar to those described in the previous section.

Some fairly "thick" crystal flakes were embedded in epoxy resin and cut by a microtome (Ultrotome LKB III) normal to the direction of the *a* axis (cf. Fig. 2). The thin slices (up to several hundred Å) were studied with transmission electron microscope techniques. The crystal fragments were sometimes found to show a stepped contour along the direction of the *c* axis. The height of the steps was found to be 12–14 Å. It is tempting to associate this appearance with the observation in Fig. 2 and with the character of the structure which is built up of layers 13.6 Å thick (cf. below).

At a later stage of the work the technique introduced by Spring Thorpe [6] was successfully applied to obtain "three-dimensional" crystals. A mixture of fine-grained silicon, red phosphorus and tin in molar ratios 1:1:10 was sealed in an evacuated silica tube. The mixture was heated to 1 150°C and then slowly cooled (10°C/hour) to room temperature. The product was treated with hot concentrated hydrochloric acid to remove the tin matrix. In this way prismatic crystals measuring several mm were obtained. The colour of the crystals was similar to that of the products described above, viz. reddish golden. While the thin crystals are transparent, the thick ones are opaque. The X-ray powder patterns of all the samples were, however, found to be identical.

Collecting of diffraction data

The X-ray powder patterns used to characterize the various preparations were taken in a Guinier–Hägg camera with monochromatized CuKα_1 radiation. Potassium chloride, $a = 6.2930$ Å, was added to the specimens as an internal standard. The flaky character of most of the samples was found to give rise to preferred orientation of the crystallites, which was obvious from the considerable variations in the relative intensities of the reflections in various samples. Such specimens gave rather different patterns when mixed with gum arabic. Table I lists a powder pattern obtained in this way.

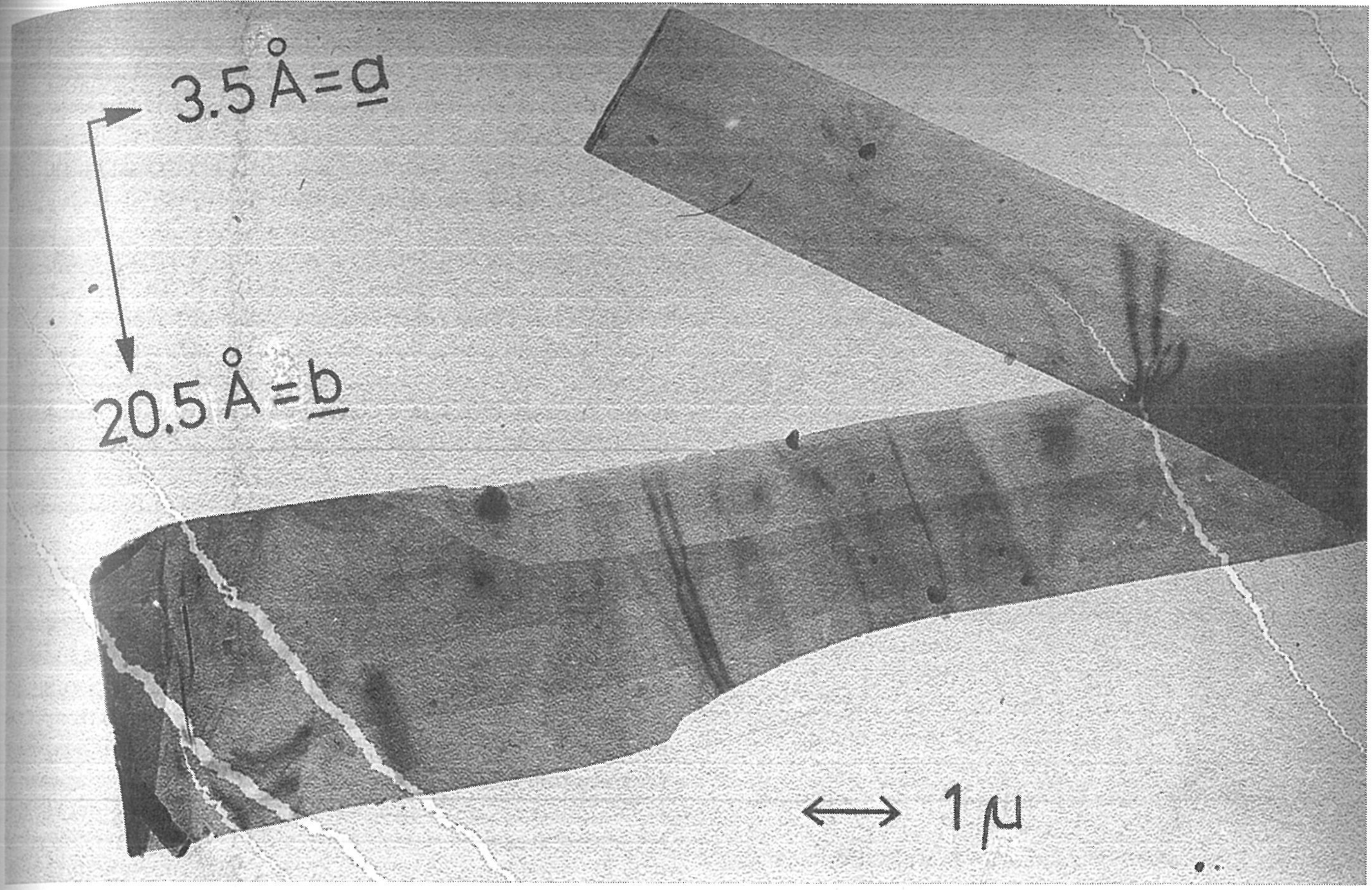

Fig. 2. Transmission electron microscope photograph of SiP crystals. The *c* axis is normal to the crystal flakes and the directions of the *a* and *b* axes indicated in the picture.

Both electron and X-ray diffraction techniques were used to collect single-crystal data for the structure determination. The very thin crystals obtained in several of the synthesis experiments were found to be well suited for studies by electron diffraction techniques. A Philips 300 M instrument was used at 100 kV, corresponding to a wavelength of 0.037 Å. The cell dimensions of silicon monophosphide were obtained by using a support of polycrystalline palladium or of thallium chloride on a carbon film as internal standard.

By transmission microscope techniques it was found that the silicon monophosphide crystal flakes often were of uniform thickness over areas of several μm^2. The flakes were transferred from the reaction tube (cf. above) in ethyl alcohol and a drop of the suspension was placed on the grid, which was normally coated with an amorphous carbon film. The flakes were found to extend in the *ab* plane. The corresponding cell parameters were found to be $a=3.51$ Å and $b=20.5$ Å. Excellent photographs of *hk*0 reflections could be obtained in this way (cf. Fig. 4). The number of reflections thus registered amounts to about 400.

The diffractogram was measured with an automatic film scanner,

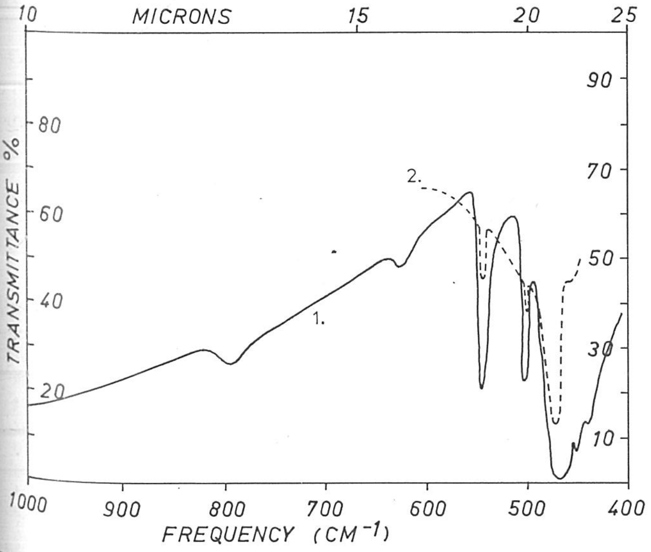

Fig. 3. IR diagrams of SiP in KBr medium. 1. this work, 2. according to Ref. [2].

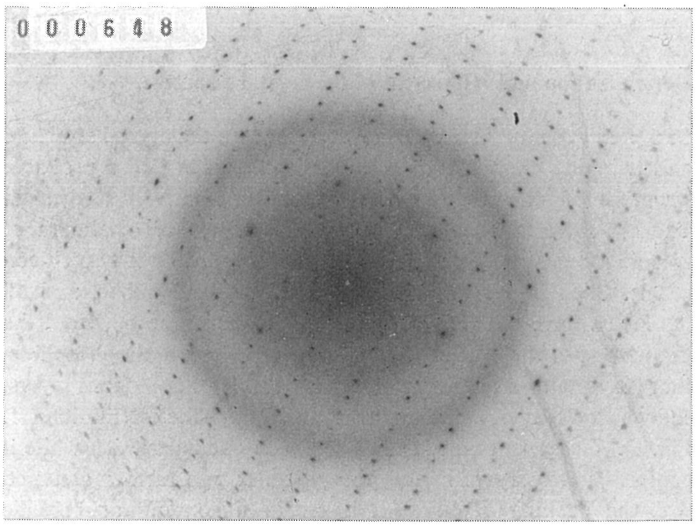

Fig. 4. Electron diffraction patterns of SiP crystal showing *hk*0 reflexions wave length 0.037 Å.

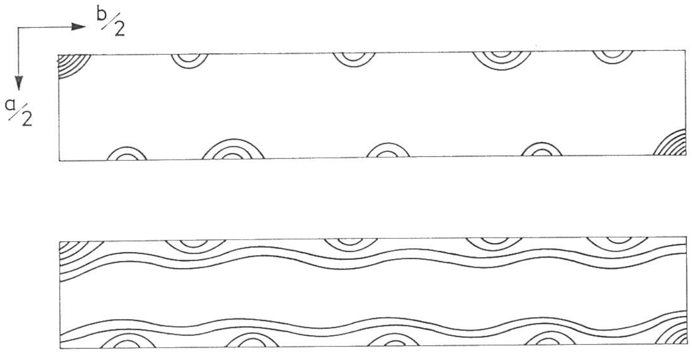

Fig. 5. Patterson maps of SiP based on *hk*0 reflections, above, 98 electron diffraction data, below, 34 X-ray reflections.

SAAB model 2 [12]. Integrated intensities were obtained by a profile analysis of diffraction spots using a procedure developed by Werner [13]. It was found possible to determine all the intensities from one single film. The relatively small variation in the electron diffraction intensities and the increased linear optical density range obtained by a second order correction term for the relative optical densities [14] made it possible to avoid using several films with different exposure times. The latter would correspond to the multiple film technique usually applied in X-ray crystallography. Furthermore, this means that no scale factor had to be determined to obtain the unique diffraction intensities.

The thin crystal flakes of silicon phosphide were found to give rather poor X-ray diffraction data. However, for the initial stages of the structure investigation such crystals had to be used for taking Weissenberg photographs in order to provide data with l indices $\neq 0$. The crystals were rotated around the a axis and the photographs were taken with Cu$K\alpha$ radiation.

As mentioned above it was eventually found possible to prepare crystals well suited for X-ray single crystal techniques by precipitation from molten tin. A transparent rectangular prism, with dimensions $0.1 \times 0.03 \times 0.02$ mm³, was used to collect three-dimensional data on a Philips PW 1100 computer-controlled single-crystal diffractometer with graphite monochromatized Cu$K\alpha$ radiation. The 530 data points available within $\theta < 60°$ were collected with a 2 θ scan range of 2°, and the background intensity was measured at both ends of the range. The 450 reflections with $\sigma(I_{\text{net}})/I_{\text{net}} < 0.25$ were used in the subsequent calculations. No absorption correction was applied, being appreciably less than the statistical error of measurement.

Determination and refinement of the crystal structure

In a previous study by the present author on the crystal structure and twinning character of silicon monoarsenide [15] a probable structure of silicon monophosphide was tentatively suggested. The structure of the arsenide contains layers of octahedra of arsenic atoms, every octahedron containing inside it two silicon atoms. Such layers are stacked on top of each other, and all the layers have the same orientation. It was proposed, from the knowledge of the unit cell dimensions of silicon monophosphide, that the structure of the latter would consist of analogous layers, every second layer, however, being in an opposite orientation (cf. Fig. 6). The repeat unit in the arsenide is one layer thick while it comprises two layers in the phosphide. It was further assumed that the packing of adjacent layers in silicon monophosphide would result in a fit similar to that between the somewhat puckered nets of arsenic atoms found in SiAs. The arrangement thus arrived at as a probable structure of SiP lacked a centre of symmetry. An experimental investigation of the actual material gave clear evidence of the substance being piezoelectric.

The data obtained from the electron diffraction experiments supplemented with the Weissenberg data were used to test the validity of the hypothetic structure. The *hk*0 electron diffraction data were used for calculation of two Patterson projections along the c axis. The number of independent reflections included in the summation amounted to 120. Two sets of Fourier coefficients were used viz. $I^2(hkl)$ [16] and $1/d \cdot I(hkl)$ [17]. The results differ very little from each other mainly because of the small variance in the intensity distribution. Fig. 5*a* shows the result of the first summation and for comparison Fig. 5*b* reproduces the appearance of the Patterson projection derived from the observed *hk*0 X-ray diffraction data. It was possible to associate the remarkably well resolved peaks of Fig. 5*a* with distances between atoms arranged in the way postulated above. The z parameters of the atoms thus located in the *ab* projection had to be derived from the Weissenberg data. A Patterson projection on the *bc* plane calculated from these data gave peaks, which were also in agreement with the hypothetic structure.

Attempts to use the electron diffraction data for refinement of the parameters were not successful. It was not even possible to obtain a reasonably good electron potential map from this material. On the other hand, the Weissenberg data could be used for some refinement of the y and z parameters.

The results so far obtained seemed to confirm the validity of the hypothetic structural model, but the quality of the experimental data did not allow a refinement of the crystal structure to be performed. The preparation of good single crystals of silicon mono-

Table II. *Crystal structure data of SiP*

$a = 3.5118 \pm 4$ Å
$b = 20.488 \pm 2$ Å
$c = 13.607 \pm 4$ Å
Space group: $Cmc2_1$
All atoms occupy 4 (a) positions
$0, y, z;\quad 0, y, \tfrac{1}{2}+z;\quad \tfrac{1}{2}, \tfrac{1}{2}+y, z;\quad \tfrac{1}{2}, \tfrac{1}{2}-y, \tfrac{1}{2}+z$

Fractional atomic coordinates

Atom	x	y	z
Si(1)	0	0.170695	0.262186
Si(2)	0	0.060176	0.219992
Si(3)	0	0.435930	0.319717
Si(4)	0	0.432388	0.148270
Si(5)	0	0.794999	0.163113
Si(6)	0	0.798080	0.335220
P(1)	0	0.999828	0.362513
P(2)	0	0.230929	0.120265
P(3)	0	0.344322	0.413142
P(4)	0	0.541255	0.117960
P(5)	0	0.689588	0.364728
P(6)	0	0.885976	0.069940

Anisotropic thermal parameters

$T = \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Si(1)	0.020240	0.000193	0.001048	0	0	0.000245
Si(2)	0.014630	0.000168	0.001065	0	0	−0.000128
Si(3)	0.027900	0.000307	0.001301	0	0	−0.000103
Si(4)	0.012499	0.000252	0.000374	0	0	0.000009
Si(5)	0.017672	0.000226	0.000428	0	0	−0.000284
Si(6)	0.024972	0.000245	0.001189	0	0	0.000392
P(1)	0.020108	0.000248	0.000959	0	0	−0.000310
P(2)	0.017377	0.000342	0.001201	0	0	−0.000198
P(3)	0.007912	0.000342	0.000971	0	0	−0.000084
P(4)	0.012112	0.000148	0.001195	0	0	0.000348
P(5)	0.026086	0.000246	0.000792	0	0	0.000040
P(6)	0.025447	0.000212	0.000552	0	0	0.000070

Table III

H	K	L	FO	FC
0	2	0	10	11
0	4	0	59	54
0	6	0	33	29
0	8	0	162	155
0	10	0	0	3
0	12	0	21	20
0	14	0	54	56
0	16	0	93	91
0	18	0	91	90
0	20	0	49	49
0	22	0	59	59
0	24	0	0	8
1	1	0	0	5
1	3	0	60	57
1	5	0	102	96
1	7	0	0	2
1	9	0	194	189
1	11	0	32	33
1	13	0	0	0
1	15	0	0	9
1	17	0	57	56
1	19	0	59	57
1	21	0	17	14
1	23	0	32	32
2	0	0	403	391
2	2	0	0	5
2	4	0	34	33
2	6	0	16	18
2	8	0	118	116
2	10	0	0	1
2	12	0	16	15
2	14	0	48	46
2	16	0	76	74
2	18	0	75	76
2	20	0	43	41
3	1	0	0	1
3	3	0	30	33
3	5	0	56	59
3	7	0	0	0
3	9	0	123	122
3	11	0	22	23
3	13	0	0	0
3	15	0	0	7
3	17	0	41	41
4	0	0	224	216
4	2	0	0	0
4	4	0	15	18
4	6	0	0	10
0	0	1	0	0
0	2	1	34	31
0	4	1	17	18
0	6	1	68	65
0	8	1	108	102
0	10	1	22	20
0	12	1	93	89
0	14	1	73	73
0	16	1	121	119
0	18	1	59	59
0	20	1	87	85
0	22	1	16	13
0	24	1	63	65
1	1	1	0	12
1	3	1	138	134
1	5	1	76	70
1	7	1	0	8
1	9	1	69	67
1	11	1	217	210
1	13	1	0	3
1	15	1	18	16
1	17	1	71	69
1	19	1	136	136
1	21	1	28	29
1	23	1	63	64
2	2	1	14	18
2	4	1	0	10
2	6	1	44	43
2	8	1	79	76
2	10	1	19	16
2	12	1	74	71
2	14	1	63	59
2	16	1	100	99
2	18	1	49	49
2	20	1	70	71
3	1	1	18	10
3	3	1	69	77
3	5	1	41	43
3	7	1	17	7
3	9	1	43	43
3	11	1	146	141
3	13	1	0	2
3	15	1	17	11
3	17	1	48	49
4	0	1	0	0
4	2	1	16	11
4	4	1	0	4
4	6	1	22	25
0	0	2	128	142
0	2	2	28	26
0	4	2	55	51
0	6	2	195	187
0	8	2	148	141
0	10	2	73	70
0	12	2	97	96
0	14	2	65	64
0	16	2	75	73
0	18	2	39	36
0	20	2	61	63
0	22	2	21	20
0	24	2	0	2
1	1	2	30	33
1	3	2	177	179
1	5	2	96	92
1	7	2	48	44
1	9	2	55	54
1	11	2	36	35
1	13	2	18	16
1	15	2	36	32
1	17	2	27	27
1	19	2	41	42
1	21	2	18	16
1	23	2	89	90
2	0	2	89	88
2	2	2	14	16
2	4	2	32	33
2	6	2	129	129
2	8	2	110	106
2	10	2	54	53
2	12	2	81	78
2	14	2	55	53
2	16	2	61	61
2	18	2	30	29
2	20	2	54	53
3	1	2	22	20
3	3	2	91	102
3	5	2	53	55
3	7	2	25	26
3	9	2	35	36
3	11	2	27	24
3	13	2	18	12
3	15	2	19	23
4	0	2	47	48
4	2	2	14	10
4	4	2	0	19
4	6	2	67	74
0	0	3	0	0
0	2	3	116	118
0	4	3	87	84
0	6	3	102	95
0	8	3	48	44
0	10	3	84	83
0	12	3	61	58
0	14	3	0	9
0	16	3	50	50
0	18	3	0	10
0	20	3	113	115
0	22	3	0	17
0	24	3	19	18
1	1	3	66	69
1	3	3	91	93
1	5	3	18	21
1	7	3	65	64
1	9	3	59	57
1	11	3	48	49
1	13	3	0	1
1	15	3	110	109
1	17	3	47	48
1	19	3	29	28
1	21	3	0	7
1	23	3	30	31
2	0	3	0	0
2	2	3	73	78
2	4	3	50	57
2	6	3	69	66
2	8	3	34	34
2	10	3	64	66
2	12	3	49	47
2	14	3	0	8
2	16	3	44	41
2	18	3	0	8
2	20	3	96	97
3	1	3	39	38
3	3	3	50	55
3	5	3	0	16
3	7	3	43	42
3	9	3	43	37
3	11	3	40	33
3	13	3	0	2
3	15	3	78	76
4	0	3	0	0
4	2	3	39	45
4	4	3	30	32
4	6	3	38	39
0	0	4	223	242
0	2	4	19	19
0	4	4	107	105
0	6	4	16	14
0	8	4	34	31
0	10	4	81	82
0	12	4	46	45
0	14	4	70	68
0	16	4	52	52
0	18	4	25	26
0	20	4	59	58
0	22	4	21	20
0	24	4	0	5
1	1	4	81	84
1	3	4	70	74
1	5	4	46	48
1	7	4	91	90
1	9	4	214	213
1	11	4	29	28
1	13	4	47	43
1	15	4	50	48
1	17	4	0	16
1	19	4	27	24
1	21	4	32	32
1	23	4	16	16
2	0	4	151	161
2	2	4	0	12
2	4	4	71	73
2	6	4	0	10
2	8	4	27	23
2	10	4	66	64
2	12	4	35	36
2	14	4	59	56
2	16	4	44	43
2	18	4	19	21
2	20	4	48	49
3	1	4	47	53
3	3	4	41	46
3	5	4	28	31
3	7	4	54	59
3	9	4	141	143
3	11	4	24	20
3	13	4	33	30
3	15	4	34	33
4	0	4	87	91
4	2	4	0	7
4	4	4	44	41
0	0	5	0	0
0	2	5	41	40
0	4	5	75	75
0	6	5	92	92
0	8	5	65	62
0	10	5	108	107
0	12	5	56	56
0	14	5	111	107
0	16	5	87	84
0	18	5	58	60
0	20	5	97	97
0	22	5	35	38
1	1	5	79	82
1	3	5	105	111
1	5	5	59	61
1	7	5	144	146
1	9	5	71	71
1	11	5	53	51
1	13	5	0	15
1	15	5	0	12
1	17	5	49	49
1	19	5	89	91
1	21	5	38	38
1	23	5	34	36
2	0	5	0	0
2	2	5	32	32
2	4	5	54	58
2	6	5	68	72
2	8	5	50	49
2	10	5	87	87
2	12	5	49	46
2	14	5	88	89
2	16	5	68	70
2	18	5	50	51
2	20	5	79	81
3	1	5	53	51
3	3	5	69	70
3	5	5	40	40
3	7	5	92	96
3	9	5	48	46
3	11	5	31	33
3	13	5	0	11
3	15	5	0	8
4	0	5	0	0
0	0	6	27	28
0	2	6	17	21
0	4	6	100	102
0	6	6	81	83
0	8	6	90	91
0	10	6	131	131
0	12	6	52	50
0	14	6	103	105
0	16	6	99	99
0	18	6	61	62
0	20	6	67	66
0	22	6	22	21
1	1	6	118	121
1	3	6	130	133
1	5	6	123	127
1	7	6	38	37
1	9	6	70	72
1	11	6	25	24
1	13	6	0	4
1	15	6	70	71
1	17	6	131	134
1	19	6	86	88
1	21	6	48	49
2	0	6	0	22
2	2	6	0	16
2	4	6	78	78
2	6	6	64	66
2	8	6	70	73
2	10	6	105	107
2	12	6	39	41
2	14	6	84	86
2	16	6	80	83
2	18	6	51	52
3	1	6	79	80
3	3	6	87	87
3	5	6	85	83
3	7	6	25	28
3	9	6	47	49
3	11	6	0	16
3	13	6	0	1
0	0	7	0	0
0	2	7	104	107
0	4	7	17	17
0	6	7	151	158
0	8	7	42	44
0	10	7	95	97
0	12	7	59	59
0	14	7	64	64
0	16	7	72	74
0	18	7	21	19
0	20	7	26	23
0	22	7	45	48
1	1	7	132	134
1	3	7	98	98
1	5	7	88	89
1	7	7	0	10
1	9	7	28	30
1	11	7	18	19
1	13	7	41	40
1	15	7	43	45
1	17	7	34	32
1	19	7	36	35
1	21	7	24	24
2	0	7	0	0
2	2	7	86	85
2	4	7	0	14
2	6	7	128	127
2	8	7	34	36
2	10	7	79	80
2	12	7	48	50
2	14	7	52	53
2	16	7	62	62
2	18	7	0	16
3	1	7	90	88
3	3	7	67	66
3	5	7	63	61
3	7	7	0	8
3	9	7	0	19
3	11	7	0	12
3	13	7	28	28
0	0	8	71	68
0	2	8	48	46
0	4	8	101	102
0	6	8	56	58
0	8	8	0	14
0	10	8	38	39
0	12	8	62	63
0	14	8	35	33
0	16	8	63	65
0	18	8	0	9
0	20	8	27	28
1	1	8	64	63
1	3	8	28	32
1	5	8	39	39
1	7	8	34	34
1	9	8	0	12
1	11	8	22	18
1	13	8	148	155
1	15	8	42	44
1	17	8	64	67
1	19	8	39	40
1	21	8	0	4
2	0	8	56	54
2	2	8	39	38
2	4	8	87	83
2	6	8	49	47
2	8	8	0	11
2	10	8	33	32
2	12	8	52	52
2	14	8	24	28
2	16	8	54	55
3	1	8	45	44
3	3	8	27	19
3	5	8	29	27
3	7	8	26	23
3	9	8	0	8
3	11	8	0	13
0	0	9	0	0
0	2	9	97	97
0	4	9	87	87
0	6	9	32	33
0	8	9	40	40
0	10	9	58	61
0	12	9	41	47
0	14	9	18	18
0	16	9	67	71
0	18	9	0	7
0	20	9	0	8
1	1	9	33	33
1	3	9	0	9
1	5	9	36	39
1	7	9	88	89
1	9	9	0	15
1	11	9	0	3
1	13	9	42	43
1	15	9	0	11
1	17	9	21	21
1	19	9	78	82
2	0	9	0	0
2	2	9	80	79
2	4	9	72	71
2	6	9	30	28
2	8	9	31	34
2	10	9	52	50
2	12	9	40	39
2	14	9	20	16
2	16	9	59	59
3	1	9	23	22
3	3	9	0	5
3	5	9	30	28
3	7	9	67	62
3	9	9	0	10
0	0	10	85	83
0	2	10	35	35
0	4	10	35	36
0	6	10	82	81
0	8	10	68	67
0	10	10	149	155
0	12	10	0	20
0	14	10	45	47
0	16	10	63	66
0	18	10	0	5
1	1	10	86	82
1	3	10	33	33
1	5	10	60	60
1	7	10	82	82
1	9	10	23	27
1	11	10	0	1
1	13	10	0	
1	15	10	20	1
1	17	10	26	2
1	19	10	86	8
2	0	10	69	6
2	2	10	31	2
2	4	10	32	2
2	6	10	71	6
2	8	10	58	5
2	10	10	130	13
2	12	10	16	1
2	14	10	42	3
3	1	10	63	5
3	3	10	21	2
3	5	10	44	4
3	7	10	61	5
0	2	11	114	11
0	4	11	47	4
0	6	11	83	7
0	8	11	61	6
0	10	11	89	8
0	12	11	26	2
0	14	11	53	5
0	16	11	25	2
0	18	11	23	2
1	1	11	85	8
1	3	11	70	6
1	5	11	41	3
1	7	11	63	6
1	9	11	39	4
1	11	11	94	9
1	13	11	60	5
1	15	11	0	
1	17	11	35	3
2	0	11	0	
2	2	11	97	9
2	4	11	45	4
2	6	11	68	6
2	8	11	50	5
2	10	11	78	7
2	12	11	18	2
3	1	11	61	5
3	3	11	51	4
0	0	12	32	3
0	2	12	66	6
0	4	12	88	8
0	6	12	93	9
0	8	12	41	4
0	10	12	46	4
0	12	12	28	2
0	14	12	50	5
0	16	12	36	3
1	1	12	0	2
1	3	12	57	5
1	5	12	48	4
1	7	12	34	3
1	9	12	27	2
1	11	12	34	3
1	13	12	156	15
1	15	12	20	21
2	0	12	27	2
2	2	12	54	5
2	4	12	77	7
2	6	12	82	7
2	8	12	38	3
2	10	12	41	3
0	0	13	0	
0	2	13	73	7
0	4	13	45	4
0	6	13	92	91
0	8	13	24	2
0	10	13	23	2
0	12	13	20	2
0	14	13	36	3
1	1	13	43	44
1	3	13	65	6
1	5	13	92	9
1	7	13	44	4
1	9	13	26	2
1	11	13	29	3
1	13	13	66	6
2	6	13	78	76
2	8	13	23	21
2	10	13	21	20

phosphide from molten tin, however, did eventually make it possible to obtain excellent starting data for that stage of the structural study.

The net intensities, obtained from the automatic single crystal diffractometer, were corrected for Lorentz and polarization effects with a modification of program DATAP2 for the Stockholm IBM 360/75 computer.

The crystal structure was then refined with the atomic scattering curves for Si^0 and P^0 [18] with the real part of the anomalous dispersion included. The full-matrix least squares program LALS minimizing $\Sigma w(|F_{obs}| - |F_{calc}|)^2$ was used. After four cycles of

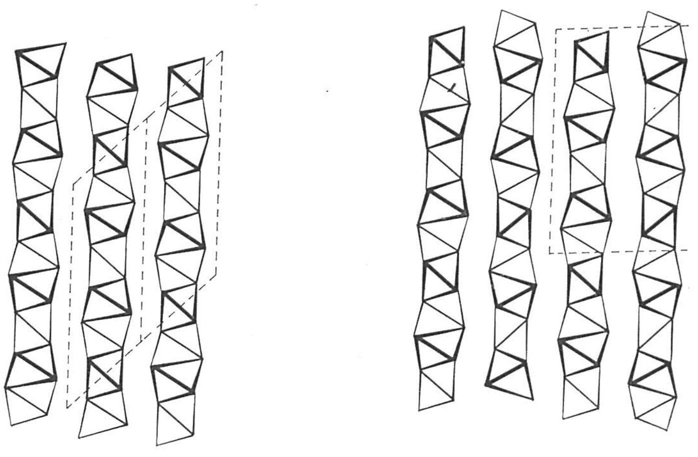

Fig. 6. Relationship between the monoclinic SiAs type and the orthorhombic SiP structures. Only the As_6 and P_6 octahedra are shown.

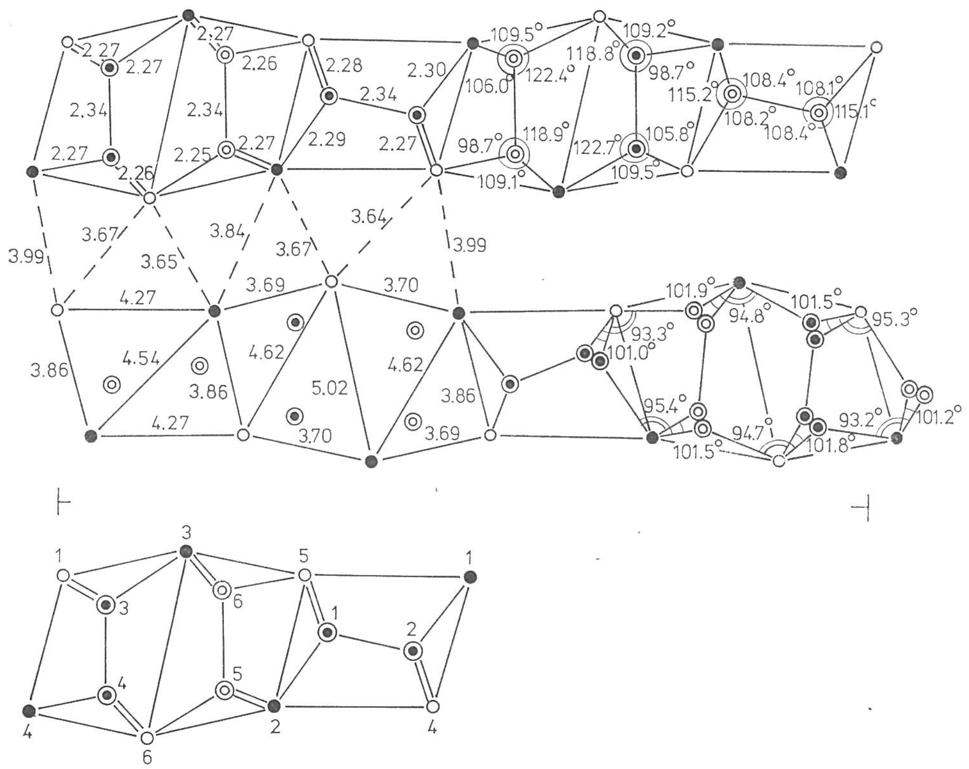

Fig. 7. The crystal structure of SiP projected along [100] with atomic numbering and interatomic distances and angles.

refinement with isotropic temperature factors an R value of 4.2% was obtained, and the structural parameters were those reported in [19]. In a subsequent refinement, when all atoms were allowed anisotropic temperature factors with symmetry requirements $B_{12}=0$ and $B_{13}=0$ [20], the R value decreased in four cycles to 3.6%. The atomic parameters from the last cycle are listed in Table II, and the structure factors are presented in Table III. The programs used in this refinement are briefly described in a paper by Nord [21].

Description and Discussion

The crystal structure of silicon monophosphide thus arrived at is in agreement with the hypothetic structure postulated from the similarity with the SiAs type structure [15]. This is illustrated in Fig. 6. The layer character is reflected in the flaky appearance of the crystals, which grow preferentially parallel to the layers, i.e. in the (001) plane. This is also a characteristic cleavage plane of the crystals.

The layers are composed of two slightly puckered triangular nets of phosphorus atoms, arranged on top of each other in such a way that the atoms form somewhat distorted octahedra which are mutually connected by sharing edges. Two silicon atoms are situated in each P_6 octahedron (cf. Fig. 7). In this way all silicon atoms possess a tetrahedral environment of one silicon and three phosphorus atoms. The phosphorus atoms have a one-sided environment of three nearest neighbours, all of which are silicon atoms. The interatomic distances and angles are given in Fig. 7;

Table IV. *Coordination and interatomic distances in several silicon and phosphorus compounds*

Compound	C.N. around Si	C.N. around P	Dist. Si–Si	Dist. Si–P	Dist. P–P	Remarks	Ref.
Si (diamond)	4 Si		2.352				—
Si (distorted bcc)	4 Si		2.30–2.39				25, 29
Si (white tin type)	6 Si		2.43 2.58			4 Si 2 Si	27
P (black)		3 P			2.23 3.30–.47 3.59–.80	 Within layers Between layers	26
P (A7 arsenic type)		3 P			2.13 3.38 2.85	 Within layers Between layers	
P (simple cubic)		6 P			2.38		28
SiP(orh)	3 P+Si	3 Si	2.342	2.271	3.41–4.7 3.64–.99	Within layers Between layers	19
SiP (zinc blende type)	4 P			2.269			7
SiP_2 (pyrite type)	6 P	3 Si+P		2.36	2.16		7, 8, 9
$CdSiP_2$	4 P	2 Si+2 Cd		2.247			22
$ZnSiP_2$	4 P	2 Si+2 Zn		2.254			23
$P(SiH_3)_3$	P+3 H	3 Si		2.248		Gas phase	24
$CuSi_2P_3$ (zinc blende type)				2.27		Cu and Si statistically distributed	30

the standard deviations amount to 0.005 Å and 0.2° resp.

The crystal structure of SiP is advantageously discussed by comparisons with the structures of some other silicon and phosphorus compounds. Relevant structural data are listed in Table IV.

The Si–P distances of orthorhombic SiP are very close to those present in the zincblende type modification [7] and $CuSi_2P_3$ [30]. They are also close to the distances found in other related tetrahedral structures such as $CdSiP_2$ [22] and $ZnSiP_2$ [23] which are of the chalcopyrite type. The Si–P distance reported from an electron diffraction study of gaseous trisilyl phosphine [24] has a similar value.

In all these compounds silicon is tetrahedrally coordinated and the interatomic distances are within the rather narrow range 2.25–2.30 Å. In the pyrite type modification of SiP_2, with six-fold coordination of phosphorus around silicon, the Si–P distance is markedly longer, viz. 2.36 Å. The Si–Si distance in SiP (orh) is close to that present in the diamond-type modification of silicon and to the average value (2.37 Å) in one of the high pressure forms of the element [29]. In the latter structure, which represents a distortion of the diamond type associated with a 10% increase of the density, the distances show a considerable spread from 2.30 to 2.39 Å. Another modification of silicon obtained at very high pressures (about 150 kb) has been reported to possess a white thin structure with hexacoordination and considerably longer interatomic distances of 2.43 and 2.58 Å [27]. A wurtzite type modification of silicon has also been reported, but the unit cell dimensions are not accurately known [29].

It is interesting to note that the building unit of orthorhombic SiP, described above as a P_6 octahedron containing two silicon atoms, has a counterpart in the high pressure distorted diamond type of silicon, all the atoms in the latter course being silicons [25]. While in SiP these structural elements are joined by edges to form layers, the linking in this silicon structure is by corners in three dimensions.

The P–P distances in SiP (orh) are all rather long. The shortest distance within a layer is 3.51 Å, corresponding to the length of the *a* axis, and the maximum P–P edge of an octahedron amounts to 5.02 Å, which demonstrates the considerable degree of distortion of the P_6 octahedra. The distances between phosphorus atoms of adjacent layers range from 3.64 to 3.99 Å. Similar P–P distances are present in the chalcopyrite type structures of $CdSiP_2$ and $ZnSiP_2$.

These long P–P distances indicate a low degree of bonding and are in marked contrast to those present in the black phosphorus modification [26] which shows a coordination with three closest neighbours at about 2.23 Å. The next-nearest neighbours of this layer structure are, however, rather similar to the shortest ones in SiP (orh), viz. 3.30–3.47 Å within the layers and 3.59–3.80 Å between layers. In the phosphorus atom doublets of the pyrite-type modification of SiP_2 the contact is very short, viz. 2.16 Å.

By high pressure techniques two further phosphorous modifications have been obtained [28]. At around 85 kb the orthorhombic black type is transformed into an arsenic type (A7) structure, and upon an increase of the pressure to about 125 kb another phase transition takes place, leading to a primitive cubic modification with six coordination.

These transitions imply successive structural changes from the marked one-sided pyramidal coordination in orthorhombic black P to the less asymmetric arrangement in the arsenic form with three close neighbours at about 2.15 Å and three next nearest atoms at 2.85 Å and, finally, to the fully symmetric cubic type with six neighbours at 2.38 Å.

Acknowledgements

The author wishes to thank Professor Arne Magnéli for stimulating intere and valuable discussions. Dr Sven Westman is thanked for revising tl English text. This investigation has been supported by the Swedish Natur Science Research Council.

References

1. Biltz, W., Sitzber. Preuss. Akad. Wiss. Berlin, k. 1 *1938*, 100, 99.
2. Fritz, G. and Berkenhoff, H. O., Z. Anorg. Allgem. Chem. *1959*, 30(205.
3. Schmidt, P. F. and Stickler, R., J. Electrochem. Soc. *1964*, 111, 1188.
4. O'Keeffe, T. W., Schmidt, P. F. and Stickler, R., J. Electrochem. So *1965*, 112, 878.
5. Beck, C. G. and Stickler, R., J. Appl. Phys. *1966*, 37, 4683.
6. Spring Thorpe, A. J., Mat. Res. Bull. *1969*, 4, 125.
7. Osugi, J., Namikawa, R. and Tanaka, Y., Rev. Phys. Chem. Japa *1966*, 36, 35.
8. Wadsten, T., Acta Chem. Scand. *1967*, 21, 1374.
9. Donohue, P. C., Siemons, W. J. and Gillson, J. L., J. Phys. Chem Solids *1968*, 29, 807.
10. Schubert, K., Dörre, E. and Günzel, D., Naturwiss. *1954*, 41, 448.
11. Wadsten, T., Acta Chem. Scand. *1965*, 19, 1232.
12. Abrahamsson, S., J. Sci. Instr. *1966*, 43, 931.
13. Werner, P.-E., Arkiv Kemi *1969*, 31, 505.
14. Werner, P.-E., J. Phys. E.; Sci. Instrum. *1969*, 4, 485.
15. Wadsten, T., Acta Chem. Scand. *1969*, 23, 331.
16. Cowley, J., Progress in materials science *1967*, 13.
17. Vainshtein, B. K., Structure Analysis by Electron Diffraction, Pergamo Press, U.K. 1964.
18. International Tables for X-Ray Crystallography. The Kynoch Press U.K. 1962.
19. Wadsten, T., Chem. Commun. Univ. Stockholm No. VII, 1973.
20. Peterse, W. J. A. M. and Palm, J. H., Acta Cryst. *1966*, 20, 147.
21. Nord, A. G., Chem. Commun. Univ. Stockholm No. XV, 1973.
22. Abrahams, S. C. and Bernstein, J. L., J. Chem. Phys. *1971*, 55, 796.
23. Abrahams, S. C. and Bernstein, J. L., J. Chem. Phys. *1970*, 52, 5607.
24. Beagley, B., Robiette, A. G. and Sheldrick, G. M., J. Chem. Soc. A *1968*, 3002.
25. Kasper, J. S. and Richards, S. M., Acta Cryst. *1964*, 17, 752.
26. Brown, A. and Rundqvist, S., Acta Cryst. *1965*, 19, 684.
27. Jamieson, J. C., Science *1963*, 139, 762.
28. Jamieson, J. C., Science *1963*, 139, 1291.
29. Wentorf, R. H., Jr and Kasper, J. S., Science *1963*, 139, 338.
30. Folberth, O. G. and Pfister, H., Acta Cryst. *1961*, 14, 325.

Department of Inorganic Chemistry
Arrhenius Laboratory
University of Stockholm
Fack
S-104 05 Stockholm, Sweden