

The Structure of a High-temperature Polymorph of V_4As_3

ROLF BERGER

Institute of Chemistry, University of Uppsala, Box 531, S-751 21 Uppsala, Sweden

The crystal structure of a high-temperature modification of V_4As_3 has been determined using single-crystal methods. The symmetry is monoclinic (space group $C2/m$), and the compound is isotopic with Cr_4As_3 . The cell dimensions are: $a = 13.725 \text{ \AA}$, $b = 3.393 \text{ \AA}$, $c = 9.230 \text{ \AA}$, $\beta = 100.52^\circ$. The two polymorphs are structurally related and can be described in terms of different arrangements of a common structural unit.

Several intermediate phases in the vanadium-arsenic system have been reported earlier, namely V_3As , V_5As_2 , V_4As_2 , VAs, and VAs₂, and indications are given as to the presence of still more.¹⁻⁵ They were all prepared by direct combination of the elements in sealed silica tube syntheses.

In a general survey on the metal-rich part of this system using the same technique, the existence of these phases has been confirmed. In addition, a phase of composition V_3As_2 has been found. It is probably tetragonal, space group $P4/m$, $Z = 4$, with the axes $a = 9.419 \text{ \AA}$ and $c = 3.340 \text{ \AA}$. A crystal structure determination is in progress.

In the present study, the work has been extended to higher temperatures than those attainable in silica tube synthesis, by means of an argon arc furnace, and a high-temperature modification of V_4As_3 has thus been discovered. The crystal structure determination and refinement of this phase is described, and the structural relationship between the two polymorphs is discussed.

EXPERIMENTAL

Preparation. An alloy with the nominal composition VAs_{0.98} was prepared by reacting turnings from arc-melted vanadium (Materials Research Corp., claimed purity 99.95 %) and

arsenic (Koch-Light Laboratories Ltd., claimed purity better than 99.99 %) in a sealed evacuated silica ampoule. The vanadium, which was contained in an alumina boat to inhibit reaction with the silica, was placed at one end of the tube and heated to 1000 °C. The arsenic, which had previously been freed from superficial oxide by means of gentle sublimation *in vacuo*, was kept at 550 °C at the other end of the tube during the synthesis to avoid too high arsenic pressure. After 20 days the product was allowed to cool. All the arsenic had by then reacted. A powder photograph showed the presence of VAs and the orthorhombic V_4As_3 . Part of the sintered product was arc-melted in an atmosphere of purified argon. Powder diffraction analysis of the final alloy showed diffraction lines of a new phase in addition to those of VAs. The lines of the orthorhombic V_4As_3 had disappeared completely. The specimen contained several needle-shaped, mostly intergrown crystals. The crystal picked for collecting the intensity data was a very well shaped parallelepiped of the dimensions $0.104 \times 0.026 \times 0.026 \text{ mm}$.

X-Ray investigations. The cell dimensions were determined with a Guinier-Hägg type focusing camera, using strictly monochromatic $CrK\alpha_1$ radiation [$\lambda(CrK\alpha_1) = 2.28962 \text{ \AA}$] and germanium ($a = 5.65771 \text{ \AA}$) as internal calibration standard. The powder photograph was indexed using approximate cell dimensions obtained from preliminary Weissenberg and rotation photographs. Powder diffraction data from a least-squares refinement are given in Table 1.

The intensity data were recorded on a computer-controlled Stoe-Philips four-circle diffractometer using graphite monochromatized $MoK\alpha$ radiation and a NaI scintillation detector. Reflexions from a quarter of a sphere in reciprocal space were recorded to a maximum in 2θ of 80° using a $\theta - 2\theta$ step-scan procedure. Instrumental stability and crystal setting were checked using three standard reflexions re-measured every 50 reflexions.

Calculations. The calculations were performed on an IBM 370/155 or an IBM 1800 computer using programs listed in Ref. 6. Absorption corrections were applied to the intensity data

using six limiting faces of the forms {100}, {010} and {001}. The crystal was 0.104 mm along the <010>-direction. The minimum and maximum transmission factors were 0.349 and 0.477 with a calculated linear absorption coefficient of 334 cm⁻¹.

DETERMINATION OF THE STRUCTURE

The preliminary data obtained from Weissenberg films indicated a centered monoclinic symmetry. The unit cell dimensions were similar to those of Cr₄As₃,⁷ and the cell volume was very nearly one half of that of the orthorhombic V₄As₃.⁸ It was therefore suspected that the new vanadium arsenide might be a high-temperature modification of V₄As₃. This hypothesis was substantiated by an experiment, where the arc-melted product was heated in a sealed evacuated silica tube at 1050°C for seven days. Powder diffraction analysis showed that the monoclinic phase had disappeared completely and was replaced by the orthorhombic V₄As₃. In the following, the orthorhombic low-temperature form is denoted α -V₄As₃ and the monoclinic high-temperature form β -V₄As₃.

The structure refinement of β -V₄As₃ was performed by a full-matrix least-squares method. Space-group symmetry Cm was assumed, and the starting values for the coordinates were taken from the structure of Cr₄As₃.⁷ Initially, the following parameters were refined: 1 scale factor, 26 positional parameters, and 14 isotropic

Table 1. Powder diffraction data for β -V₄As₃ as measured with a Guinier-Hägg camera, using CrK α_1 radiation.

<i>h k l</i>	<i>Q</i> × 10 ⁵ (Å ⁻²)	Int.	<i>d</i> _{obs} (Å)
	obs.	calc.	
0 0 1	1 214	1.9	
2 0 0	2 197	0.3	
-2 0 1	2 815	0.0	
2 0 1	4 007	0.0	
0 0 2	4 852	4 858	Vvw
-2 0 2	5 861	0.3	
2 0 2	8 247	w	3.8
4 0 0	8 786		3.0
	8 792	w	3.372
-4 0 1	8 808		2.6
1 1 0	9 237	9 236	Vw
-1 1 1	10 147 ^a	10 153	Vw
1 1 1	10 747	10 749	w
0 0 3	10 928	10 929	m
4 0 1	11 193	11 194	w
-4 0 2	11 255	11 258	m

<i>h k l</i>	<i>Q</i> × 10 ⁵ (Å ⁻²)	Int.	<i>d</i> _{obs} (Å)
	obs.	calc.	
-2 0 3	11 342	11 337	Vvw
-1 1 2	13 502	13 498	Vvw
3 1 0	13 633	13 630	Vw
-3 1 1	13 945	13 949	Vst
1 1 2	14 694	14 690	Vst
2 0 3	14 922	14 915	Vvw
3 1 1	15 737	15 739	Vvw
4 0 2		16 030	0.2
-4 0 3	16 139	16 137	w
-3 1 2	16 699	16 698	w
-6 0 1		19 195	0.8
-2 0 4		19 241	1.3
-1 1 3	19 267	19 271	w
0 0 4	19 429	19 430	m
6 0 0	19 772	19 770	Vvw
3 1 2	20 278	20 277	st
-6 0 2		21 048	59.5
	21 053		st
1 1 3		21 061	11.1
-3 1 3	21 881 ^a	21 875	w
-5 1 1	22 136	22 139	m
5 1 0	22 418	22 416	w
6 0 1		22 773	1.6
4 0 3	23 299	23 295	Vvw
-4 0 4	23 453	23 445	Vvw
2 0 4	24 018	24 013	m
-5 1 2		24 291	1.6
5 1 1	25 127	25 122	m
-6 0 3	25 324	25 331	Vvw
3 1 3	27 245	27 243	w
-1 1 4		27 474	0.2
6 0 2	28 204	28 206	Vw
-5 1 3		28 872	0.5
-3 1 4	29 475	29 481	st
-2 0 5		29 574	0.0
1 1 4		29 859	0.0
5 1 2	30 255	30 256	m
0 0 5		30 360	0.9
-6 0 4	32 034	32 042	Vvw
4 0 4	32 990	32 988	Vw
-4 0 5	33 182	33 181	Vvw
-8 0 1		33 974	0.6
-7 1 1		34 723	16.0
	34 752		st
0 2 0		34 749	92.9
8 0 0		35 146	3.2
-8 0 2	35 233	35 232	w
2 0 5		35 538	19.7
	35 579		m
			1.677
3 1 4		35 596	21.1
-5 1 4		35 882	1.1
0 2 1		35 964	0.1
6 0 3	36 061	36 067	Vw
-7 1 2	36 274	36 278	Vw
3 1 4	36 635	36 639	Vw
			4.7
2 2 0		36 946	0.0
-2 2 1		37 564	0.0
5 1 3	37 806	37 819	w
-1 1 5		38 105	0.1

^a Overlapped by a monoarsenide line.

temperature factors. The atomic scattering factors were taken from Ref. 8 and the dispersion correction factors from Ref. 9. Reflexions with $|F_o|$ less than $3\sigma(|F_o|)$ were given zero weight, which reduced the material from 1533 to 1247 independent reflexions. The remaining reflexions were weighted according to the formula

$$w^{-1} = \sigma^2 + (0.009|F_o|)^2$$

where σ is based on counting statistics. The refinement converged to an R -value of 0.029, where

$$R = \sum |F_c| - |F_o| / \sum |F_o|$$

Extinction correction according to Coppens and Hamilton¹⁰ was tried, but the strongest reflection, (020), remained much weaker than the calculated value. The (020) reflection was then excluded from the refinement, which thus converged to an R -value of 0.025. Anisotropic temperature factors were finally introduced. The convergence was very slow, and the refinement was stopped after seven cycles at which an R -value of 0.016 was obtained. An inspection of the correlation matrix showed that there were extremely strong correlations (up to 0.98) between the parameters. The values of the positional parameters indicated that the structure was very nearly centrosymmetric, which would cause this behaviour. A second series of refinements based on the centrosymmetric $C2/m$ space-group symmetry was then performed. The refinements converged rapidly, and the final R -values obtained were 0.028 and 0.017, for isotropic and anisotropic thermal parameters, respectively (1189 reflexions).

Table 2. Structure data for β -V₄As₃, including anisotropic thermal parameters β_{ij} . The form of the temperature factor is $\exp[-\beta_{11}h^2 - \cdots - \beta_{12}hk - \cdots]$. Space group $C2/m$, $Z = 4$, $a = 13.7251(5)$ Å, $b = 3.3928(2)$ Å, $c = 9.2297(4)$ Å, $\beta = 100.521(3)^\circ$.

Atom	Position	x	y	z	$\beta_{11} \times 10^5$	$\beta_{22} \times 10^5$	$\beta_{33} \times 10^5$	$\beta_{12} \times 10^5$	$\beta_{13} = \beta_{23}$
V(1)	$2a$	0	0	0	73(3)	1335(49)	115(6)	9(3)	0
V(2)	$4i$	0.65796(4)	0	0.44440(5)	68(2)	1220(35)	139(4)	19(2)	0
V(3)	$4i$	0.22512(4)	0	0.17747(6)	59(2)	1633(38)	279(5)	21(3)	0
V(4)	$4i$	0.43820(4)	0	0.27309(5)	55(2)	1108(33)	155(4)	20(2)	0
V(5)	$2c$	0	0	1/2	45(2)	1587(50)	84(5)	9(3)	0
As(1)	$4i$	0.06945(2)	0	0.26623(3)	65(1)	1084(21)	106(3)	19(1)	0
As(2)	$4i$	0.35916(2)	0	0.01043(3)	92(1)	1092(21)	130(3)	27(1)	0
As(3)	$4i$	0.82122(2)	0	0.34827(3)	62(1)	951(21)	148(3)	17(1)	0

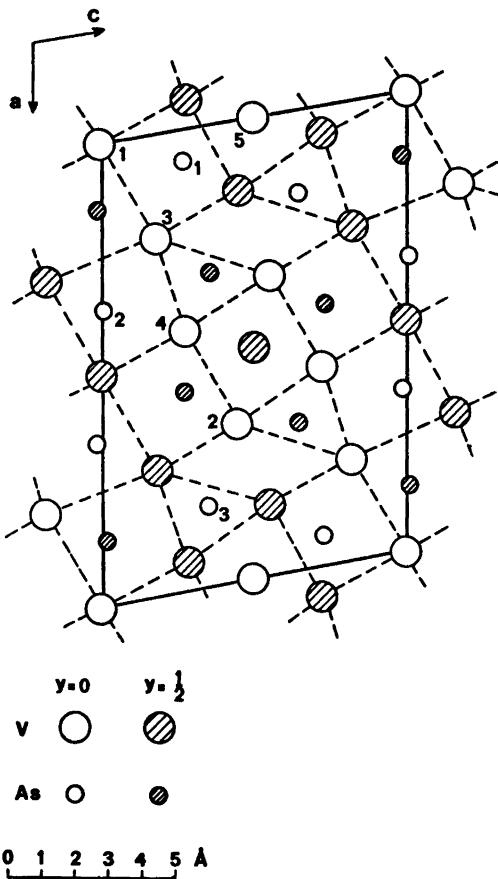


Fig. 1. The crystal structure of β -V₄As₃ projected on (010).

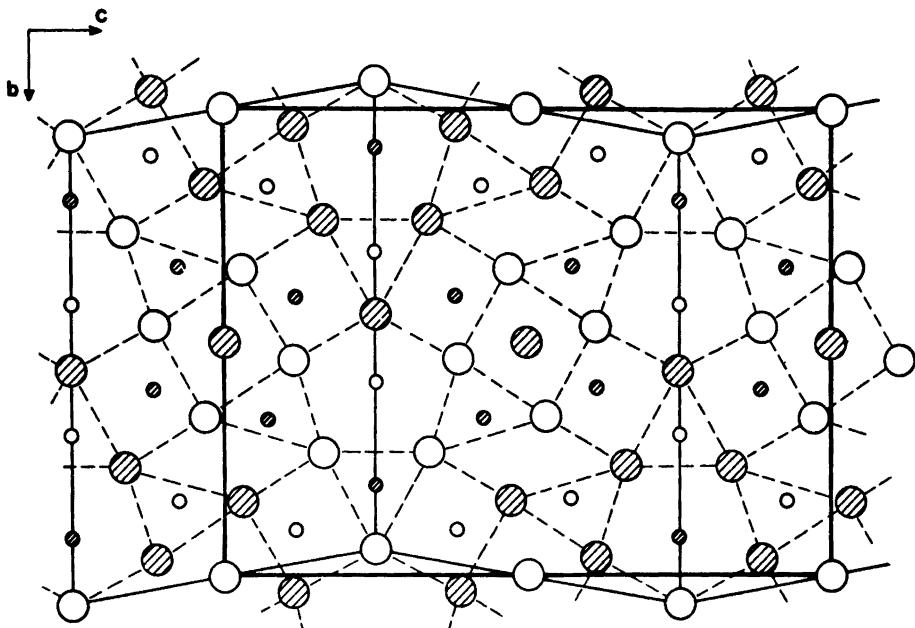


Fig. 2. The α - V_4As_3 structure projected on (100). Sub-unit arrangement indicated by thin full lines. Notation similar to Fig. 1 (Atoms at $x=0$ and $x=\frac{1}{2}$).

The agreement is very good for both the Cm and the $C2/m$ refinements, and it seems very difficult to reach a decisive conclusion as to the correct choice of space-group symmetry. An application of the Hamilton test¹¹ would probably not be valid, since uncorrected systematic errors are likely to contribute considerably to the differences between F_o and F_c . Furthermore, the strong correlations among the parameters in Cm symmetry indicate that the least-squares refinement procedure is less satisfactory, and the standard deviations are about ten times greater for the lower symmetry. The final structure is accordingly described in the terms of space-group $C2/m$ symmetry as presented in Table 2. The observed and calculated structure factors are listed in Table 3.

DESCRIPTION AND DISCUSSION

A projection of the β - V_4As_3 structure along the b -axis is illustrated in Fig. 1. The coordination of vanadium around arsenic is essentially trigonal prismatic. The coordination numbers are 6, 7, and 8 for As(2), As(1), and As(3), respectively. The structure may be considered

isotypic with Cr_4As_3 , although Baurecht, Boller and Nowotny⁷ used a non-centrosymmetric description.

It is interesting to compare the structural data for the two V_4As_3 polymorphs. The cell parameters for α - V_4As_3 as determined by the author are:

$$a = 3.4139(2) \text{ \AA}; b = 13.6798(7) \text{ \AA}; c = 18.0598(11) \text{ \AA}; V = 843.4 \text{ \AA}^3.$$

Thus, the cell-volume of β - V_4As_3 (422.6 \AA^3) is only slightly more than half of that of the low-temperature form. Both polymorphs can formally be described on a basis of different arrangement of a common sub-unit as depicted in Fig. 2. The sub-unit constitutes one unit cell of the β -form, while the unit cell of the α -form is composed of two sub-units, one being the mirror image of the other one. Consequently, the main differences between the two structures appear at the boundaries between the sub-units. The As(2) site in the β - V_4As_3 structure corresponds to two sites in α - V_4As_3 , both of coordination number six. One retains the prismatic coordination while the other one is

Table 3. Observed and calculated structure factors ($\times 10$) for β -V₄As₃. F_o -values for weak reflexions not included in the refinement are omitted from the table. The columns are h , l , $|F_o|$ and $|F_c|$.

H, O, L	2	5	2281	2235	-8	11	715	713	-3	2	1670	1674	17	7	174	181	-13	15	296	319
0 0 118 85	2 4	5 5	153 154	205	-8 11	715	713	-3 1	2	1670	1674	17 7	174	181	-13 15	215	202	69	341	352
0 0 130 614	9 8	5 5	596 593	205	-2 11	414	416	3 2	2	2471	2522	19 7	277	283	-7 15	340	324	75	332	324
0 0 1040 1032	10 10	1160 1169	1845	1845	-2 11	1843	1845	5 2	1567	1566	-23 8	279	244	-5 15	329	323	94	329	323	
0 0 898 907	12 12	766 771	213	213	-2 11	311	313	7 2	682	588	-17 8	88	808	-10 15	155	155	107	155	155	
0 0 1009 1022	14 14	405 409	397	396	-8 11	311	313	9 2	930	944	-13 8	88	808	-1 15	155	155	60	329	323	
0 0 1120 1130	18 18	582 598	433	444	-8 11	311	313	11 2	1158	1166	-11 8	88	808	-2 15	155	155	376	352	352	
0 0 795 790	20 20	582 598	355	360	-10 6	1213	1214	13 2	1750	1750	-9 7	262	229	-3 15	155	155	223	215	202	
0 0 588 577	24 24	213 194	457	457	-10 6	1213	1214	15 2	1750	1750	-7 6	816	822	-1 15	155	155	244	232	224	
0 0 392 380	26 26	1240 1184	204	204	-20 12	342	342	19 2	706	703	-5 6	377	346	-5 15	155	155	353	333	323	
0 0 599 495	18 18	109	93	23	-18 12	488	485	21 2	202	202	-3 6	301	282	-3 15	155	155	37	35	35	
0 0 695 682	21 21	218 217	218	217	-18 12	488	485	23 2	715	717	-3 6	933	920	-1 15	155	155	1327	1139	1139	
0 0 574 560	22 22	578 579	267	267	-12 6	1212	1212	24 2	686	686	-1 6	88	808	-1 15	155	155	309	309	309	
0 0 1615 604	10 10	1267 1279	192	190	-10 12	172	180	17 2	339	331	-7 6	290	290	0 0	3766	4917*	686	686	686	
0 0 340 339	8 8	621 617	192	190	-8 12	172	180	19 2	597	596	-9 6	594	596	0 0	3766	4917*	42	42	42	
0 0 1292 1292	6 6	2001 2003	151	151	-6 12	172	180	21 2	3093	3116	11 8	1751	1750	4 0	200	200	223	215	202	
0 0 797 800	16 16	1420 1420	151	151	-6 12	172	180	23 2	389	388	13 8	274	255	4 0	200	200	249	232	224	
0 0 282 264	2 2	2244 2228	197	197	-2 12	1212	1212	25 2	258	275	15 8	68	53	10 0	200	200	751	751	751	
0 0 400 407	16 16	1196 1184	204	204	-2 12	1212	1212	27 2	1416	1410	-21 9	442	434	10 0	200	200	838	839	839	
0 0 444 449	14 14	1212 1200	197	197	-2 12	1212	1212	29 2	1434	1435	-19 9	239	224	12 0	200	200	1204	1204	1204	
0 0 596 577	17 17	358 359	326	325	-2 12	1212	1212	31 2	308	308	13 8	68	53	12 0	200	200	1166	1175	1175	
0 0 169 169	8 8	1799 1796	1281	1281	-6 12	1212	1212	33 2	166	132	-1 9	99	97	16 0	200	200	1166	1162	1162	
0 0 133 133	12 12	1281 1279	1281	1281	-12 6	1212	1212	35 2	616	617	-13 9	196	197	16 0	200	200	531	519	519	
0 0 865 876	14 14	131 130	30	30	-12 6	1212	1212	37 2	1212	1212	-13 9	196	197	16 0	200	200	301	301	301	
0 0 2255 2269	16 16	151 152	155	155	-16 12	1212	1212	39 2	560	566	-9 9	303	3116	11 8	1751	1750	223	215	202	
0 0 1797 800	16 16	151 152	155	155	-16 12	1212	1212	41 2	172	172	-9 9	662	672	12 0	200	200	297	281	271	
0 0 1745 1745	14 14	1212 1200	197	197	-14 12	1212	1212	43 2	305	308	15 8	572	559	18 0	200	200	330	326	326	
0 0 1745 1745	14 14	1212 1200	197	197	-14 12	1212	1212	45 2	815	829	-5 9	1405	1406	18 0	200	200	687	687	687	
0 0 1745 1745	14 14	1212 1200	197	197	-14 12	1212	1212	47 2	978	976	-1 9	999	986	12 0	200	200	337	326	326	
0 0 533 536	16 16	522 524	151	151	-2 12	1212	1212	49 2	1212	1212	-9 9	360	343	10 0	200	200	309	309	309	
0 0 231 231	14 14	1882 1879	1915	1915	-2 12	1212	1212	51 2	791	791	-11 9	950	952	-2 0	200	200	472	466	466	
0 0 1025 1016	16 16	319 318	605	605	-2 12	1212	1212	53 2	616	614	-15 9	446	446	-2 0	200	200	83	83	83	
0 0 250 250	16 16	602 600	605	605	-2 12	1212	1212	55 2	1212	1212	-17 9	397	397	-2 0	200	200	26	26	26	
0 0 198 201	8 8	358 344	1186	1186	-8 13	1212	1212	57 2	1404	1413	-13 9	171	171	-2 0	200	200	754	740	740	
0 0 1199 1220	2 2	1195 1184	1186	1186	-10 12	1212	1212	59 2	1212	1212	-19 10	10	10	-2 0	200	200	1000	987	987	
0 0 248 240	7 7	1264 1260	1260	1260	-14 12	1212	1212	61 2	265	279	-7 9	374	375	-17 10	10	10	483	483	483	
0 0 136 137	2 2	1161 1147	1147	1147	-14 12	1212	1212	63 2	1212	1212	-19 10	10	10	-2 0	200	200	1000	987	987	
0 0 2226 2233	4 4	369 358	358	358	-10 12	1212	1212	65 2	1212	1212	-21 10	10	10	-2 0	200	200	227	225	225	
0 0 2233 2233	4 4	372 372	372	372	-10 12	1212	1212	67 2	1212	1212	-19 10	10	10	-2 0	200	200	507	495	495	
0 0 170 172	10 10	1555 1560	1560	1560	-14 12	1212	1212	69 2	265	279	-7 9	374	375	-17 10	10	10	388	388	388	
0 0 623 623	10 10	829 844	844	844	-20 12	1212	1212	71 2	200	205	-9 9	419	427	-19 10	10	10	509	490	490	
0 0 283 287	2 2	227 226	226	226	-2 12	1212	1212	73 2	277	250	1 1	1454	1453	-1 10	10	10	329	324	324	
0 0 272 272	2 2	203 202	197	197	-2 12	1212	1212	75 2	393	418	1 1	910	917	-1 10	10	10	684	684	684	
0 0 274 267	18 18	368 371	371	371	-12 6	1212	1212	77 2	381	401	1 1	401	401	-7 10	10	10	1001	1000	1000	
0 0 928 925	16 16	723 719	719	719	-10 12	1212	1212	79 2	805	815	1 1	486	498	-7 10	10	10	149	149	149	
0 0 1005 1005	11 11	1100 1095	1095	1095	-12 6	1212	1212	81 2	274	254	-7 9	886	895	-7 10	10	10	1773	1794	1794	
0 0 605 631	7 7	722 717	717	717	-14 12	1212	1212	83 2	305	315	-9 9	662	679	-13 10	10	10	2916	2977	2977	
0 0 311 293	8 8	417 423	423	423	-2 12	1212	1212	85 2	441	427	-17 9	427	427	-10 10	10	10	130	130	130	
0 0 494 513	12 12	937 933	933	933	-16 12	1212	1212	87 2	1212	1212	-17 9	419	427	-10 10	10	10	175	171	171	
0 0 1157 1165	12 12	1156 1153	1153	1153	-16 12	1212	1212	89 2	1212	1212	-17 9	568	572	-13 11	11	11	558	535	535	
0 0 1324 1324	12 12	1162 1159	1159	1159	-16 12	1212	1212	91 2	245	258	-9 9	984	993	-7 11	11	11	2279	2279	2279	
0 0 1161 1162	12 12	1153 1152	1152	1152	-16 12	1212	1212	93 2	1212	1212	-17 9	568	572	-13 11	11	11	998	998	998	
0 0 1304 1305	18 18	9 9 535	535	535	1 0	986	983	15 2	1212	1212	-4 2	457	457	-13 11	11	11	522	522	522	
0 0 665 665	16 16	9 9 172	172	172	1 0	986	983	17 2	1212	1212	-4 2	457	457	-12 12	12	12	522	522	522	
0 0 118 118	12 12	9 9 172	172	172	1 0	986	983	19 2	1212	1212	-4 2	457	457	-12 12	12	12	522	522	522	
0 0 1125 1136	10 10	9 9 396	404	404	1 1	1615	1618	21 2	1212	1212	-4 2	429	429	-10 12	12	12	522	522	522	
0 0 337 321	12 12	9 9 275	275	275	1 1	175	168	23 2	1212	1212	-4 2	429	429	-10 12	12	12	522	522	522	
0 0 436 429	12 12	9 9 1400	1393	1393	1 1	1204	1204	25 2	1212	1212	-4 2	446	446	-10 12	12	12	522	522	522	
0 0 340 343	12 12	9 9 172	172	172	1 1	1204	1204	27 2	1212	1212	-4 2	446	446	-10 12	12	12	522	522	522	
0 0 444 444	12 12	9 9 172	172	172	1 1	1204	1204	29 2	1212	1212	-4 2	446	446	-10 12	12	12	522	522	522	
0 0 1161 1162	12 12	9 9 172	172	172	1 1	1204	1204	31 2	1212	1212	-4 2	446	446	-10 12	12	12	522	522	522	
0 0 1161 1162	12 12	9 9 172	172	172	1 1	1204	1204	33 2	1212	1212	-4 2	446	446	-10 12	12	12	522	522	522	
0 0 1161 1162	12 12	9 9 172	172	172	1 1	1204	1204	35 2	1212	1212	-4 2	446	446	-10 12	12	12	522	522	522	
0 0 1161 1162	12 12	9 9 172	172	172	1 1	1204	1204	37 2	1212	1212	-4 2	446	446	-10 12	12	12	522	522</td		

Table 3. Continued.

		H, S, L
729	725	720
400	400	387
117	60	356
163	162	356
125	125	356
92	82	356
446	402	356
142	422	356
509	508	356
983	993	356
671	652	356
345	323	356
523	323	356
1305	1287	356
	106	356
205	354	356
1043	1026	356
1780	1746	356
734	1802	356
307	314	356
1090	1050	356
145	129	356
	70	356
444	423	356
510	523	356
467	466	356
1662	1559	356
204	31	356
318	963	356
1027	975	356
958	303	356
298	61	356
202	134	356
	745	356
331	310	356
186	204	356
300	329	356
639	643	356
857	853	356
629	620	356
358	357	356
560	551	356
1131	1126	356
953	941	356
684	610	356
424	412	356
301	304	356
576	510	356
423	424	356
1043	1035	356
187	169	356
181	168	356
541	523	356
359	343	356
267	1581	356
1187	1153	356
165	1552	356
253	1552	356
1217	737	356
	747	356
1042	1039	356
2039	2049	356
1040	1039	356
478	477	356
1470	1480	356
104	41	356
398	396	356
1020	1019	356
337	323	356
813	813	356
180	195	356
836	839	356
360	356	356
610	638	356
1111	447	356
1121	228	356
1128	228	356
1081	981	356
625	627	356
	237	356
1541	1609	356
265	276	356
339	326	356
342	327	356
425	409	356
450	456	356
558	556	356
1111	733	356
155	160	356
447	491	356
490	491	356
204	213	356
255	250	356
185	212	356
562	107	356
809	823	356
273	275	356
408	420	356
902	107	356
711	704	356
175	175	356
1111	173	356
224	227	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
1283	1279	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	276	356
250	199	356
251	363	356
249	263	356
311	31	356
175	173	356
102	102	356
1111	173	356
224	227	356
194	212	356
275	2	

Table 4. Interatomic distances and standard deviations for β -V₄As₃ (Å). Distances shorter than 3.5 Å are listed.

V(1) - 2 As(1)	2.468 (0)	V(5) - 2 As(1)	2.513 (0)
4 As(2)	2.587 (0)	2 As(3)	2.594 (0)
2 V(3)	3.222 (0)	4 V(4)	2.708 (0)
4 V(4)	3.276 (0)	4 V(2)	2.872 (0)
2 V(1)	3.393 (0)	2 V(5)	3.393 (0)
V(2) - 2 As(1)	2.516 (0)	As(1) - V(3)	2.424 (1)
2 As(3)	2.534 (0)	V(1)	2.468 (0)
As(3)	2.556 (1)	2 V(4)	2.484 (0)
2 V(5)	2.872 (0)	V(5)	2.513 (0)
2 V(2)	3.061 (1)	2 V(2)	2.516 (0)
V(4)	3.130 (1)	2 As(2)	3.357 (0)
V(4)	3.140 (1)	2 As(1)	3.393 (0)
2 V(3)	3.260 (1)		
2 V(2)	3.393 (0)		
V(3) - As(1)	2.424 (1)	As(2) - V(4)	2.469 (1)
2 As(3)	2.519 (0)	2 V(3)	2.548 (0)
2 As(2)	2.548 (0)	2 V(1)	2.587 (0)
As(2)	2.607 (1)	V(3)	2.607 (1)
V(4)	2.897 (1)	2 As(1)	3.357 (0)
V(1)	3.222 (0)	2 As(2)	3.393 (0)
2 V(2)	3.260 (1)	2 As(2)	3.418 (1)
2 V(3)	3.393 (0)		
V(4) - As(2)	2.469 (1)	As(3) - 2 V(3)	2.519 (0)
2 As(1)	2.484 (0)	2 V(4)	2.519 (0)
2 As(3)	2.519 (0)	2 V(2)	2.534 (0)
2 V(5)	2.708 (0)	V(2)	2.556 (1)
V(3)	2.897 (1)	V(5)	2.594 (0)
V(2)	3.130 (1)	2 As(3)	3.393 (0)
V(2)	3.140 (1)		
2 V(1)	3.276 (0)		
2 V(4)	3.393 (0)		

characterized by an irregular coordination polyhedron first found in Nb₄As₃.¹² Despite this change in geometrical arrangement, no drastic change in coordination number for near neighbours is found. Only in coordination spheres more remote than the first are neighbours affected. Interatomic distances for β -V₄As₃ are given in Table 4. The interatomic distances within the sub-unit are similar for the two polymorphs, with a maximum difference of 0.1 Å, taking data for α -V₄As₃ from Ref. 5.

Common to both forms is the appearance of a body-centered cubic arrangement of some of the metal atoms, which is found in many other metal-rich compounds between transition metals and pnictides. The structure of Mo₄P₃¹³ is closely related to that of β -V₄As₃ with respect to the stacking of the triangular prismatic building blocks, but it contains no counterpart

to the body-centered cubic metal atom arrangement in β -V₄As₃, although of the same stoichiometry.

Acknowledgements. The author thanks Professor I. Olovsson for all facilities put at disposal and is also deeply grateful to Professor S. Rundqvist for his encouragement and valuable advice. Thanks are also due to various colleagues for their help with programming and instrumental operation. This work has been financially supported by the Swedish Natural Science Research Council.

REFERENCES

1. Bachmayer, K. and Nowotny, H. *Monatsh. Chem.* 86 (1955) 741.
2. Hulliger, F. *Nature* 204 (1964) 775.
3. Meissner, H.-G. and Schubert, K. *Z. Metallk.* 56 (1965) 523.

4. Boller, H. and Nowotny, H. *Monatsh. Chem.* 97 (1966) 1053.
5. Yvon, K. and Boller, H. *Monatsh. Chem.* 103 (1972) 1643.
6. Lundgren, J. O., Ed., *Crystallographic Computer Programs*, Institute of Chemistry, University of Uppsala, Uppsala 1974, UUIC-B13-4-01.
7. Baurecht, H.-E., Boller, H. and Nowotny, H. *Monatsh. Chem.* 101 (1970) 1696.
8. Hanson, H. P. et al. *Acta Crystallogr.* 17 (1964) 1040.
9. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III.
10. Coppens, P. and Hamilton, W. C. *Acta Crystallogr. A* 26 (1970) 71.
11. Hamilton, W. C. *Acta Crystallogr.* 18 (1965) 502.
12. Carlsson, B. and Rundqvist, S. *Acta Chem. Scand.* 25 (1971) 1742.
13. Rundqvist, S. *Acta Chem. Scand.* 19 (1965) 393.

Received April 9, 1974.