The Structure of a High-temperature Polymorph of V_4As_3

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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 isotypic with Cr_4As_3. The cell dimensions are: $a = 13.725$ Å, $b = 3.393$ Å, $c = 9.230$ Å, $\beta = 100.52°$. 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_3, V_4As_3, VAs, and VAs_2, 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 $a = 9.419$ Å and $c = 3.340$ Å. 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 $VAs_{0.96}$ 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 $0.104 \times 0.026 \times 0.026$ mm.

X-Ray investigations. The cell dimensions were determined with a Guinier-Hägg type focusing camera, using strictly monochromatic $CrK\alpha_1$ radiation $[\lambda(CrK\alpha_1) = 2.28962$ Å$]$ and germanium $(a = 5.65771$ Å$)$ 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 remeasured 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 Cr_4As_3,[7] and the cell volume was very nearly one half of that of the orthorhombic V_4As_3.[5] It was therefore suspected that the new vanadium arsenide might be a high-temperature modification of V_4As_3. 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 V_4As_3. In the following, the orthorhombic low-temperature form is denoted α-V_4As_3 and the monoclinic high-temperature form β-V_4As_3.

The structure refinement of β-V_4As_3 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 Cr_4As_3.[7] Initially, the following parameters were refined: 1 scale factor, 26 positional parameters, and 14 isotropic

Table 1. Powder diffraction data for β-V_4As_3 as measured with a Guinier-Hägg camera, using $CrK\alpha_1$ radiation.

$h\,k\,l$	$Q \times 10^5$ (Å^{-2}) obs.	calc.	Int. obs.	calc.	d_{obs} (Å)
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	0.7	4.540
-2 0 2		5 861		0.3	
2 0 2	8 247	8 247	w	3.8	3.482
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	4.7	3.290
-1 1 1	10 147[a]	10 153	vw	0.3	3.139
1 1 1	10 747	10 749	w	12.3	3.050
0 0 3	10 928	10 929	m	18.8	3.025
4 0 1	11 193	11 194	w	4.2	2.989
-4 0 2	11 255	11 258	m	18.4	2.981
-2 0 3	11 342	11 337	vvw	0.1	2.969
-1 1 2	13 502	13 498	vvw	10.0	2.721
3 1 0	13 633	13 630	vw	10.0	2.708
-3 1 1	13 945	13 949	vst	43.2	2.678
1 1 2	14 694	14 690	vst	63.6	2.609
2 0 3	14 922	14 915	vvw	1.8	2.589
3 1 1	15 737	15 739	vvw	2.5	2.521
4 0 2		16 030		0.2	
-4 0 3	16 139	16 137	w	15.8	2.489
-3 1 2	16 699	16 698	w	24.4	2.447
-6 0 1		19 195		0.8	
-2 0 4		19 241		1.3	
-1 1 3	19 267	19 271	w	16.7	2.278
0 0 4	19 429	19 430	m	20.6	2.269
6 0 0	19 772	19 770	vvw	4.1	2.249
3 1 2	20 278	20 277	st	89.7	2.221
-6 0 2		21 048		59.5	
	21 053		st		2.179
1 1 3		21 061		11.1	
-3 1 3	21 881[a]	21 875	w	14.6	2.138
-5 1 1	22 136	22 139	m	51.1	2.125
5 1 0	22 418	22 416	w	19.7	2.112
6 0 1		22 773		1.6	
4 0 3	23 299	23 295	vvw	4.1	2.072
-4 0 4	23 453	23 445	vvw	4.5	2.065
2 0 4	24 018	24 013	m	40.5	2.040
-5 1 2		24 291		1.6	
5 1 1	25 127	25 122	m	33.6	1.995
-6 0 3	25 324	25 331	vvw	1.7	1.987
3 1 3	27 245	27 243	w	8.1	1.916
-1 1 4		27 474		0.2	
6 0 2	28 204	28 206	vw	9.6	1.883
-5 1 3		28 872		0.5	
-3 1 4	29 475	29 481	st	100.0	1.842
-2 0 5		29 574		0.0	
1 1 4		29 859		0.0	'
5 1 2	30 255	30 256	m	17.2	1.818
0 0 5		30 360		0.9	
-6 0 4	32 034	32 042	vvw	2.4	1.767
4 0 4	32 990	32 988	vw	12.0	1.741
-4 0 5	33 182	33 181	vvw	4.1	1.736
-8 0 1		33 974		0.6	
-7 1 1		34 723		16.0	
	34 752		st		1.696
0 2 0		34 749		92.9	
8 0 0		35 146		3.2	
-8 0 2	35 233	35 232	w	19.3	1.685
2 0 5		35 538		19.7	
	35 579		m		1.677
7 1 0		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	5.5	1.665
-7 1 2	36 274	36 278	vw	5.2	1.660
3 1 4	36 635	36 639	vw	4.7	1.652
2 2 0		36 946		0.0	
-2 2 1		37 564		0.0	
5 1 3	37 806	37 819	w	14.7	1.626
-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 Hamilton [10] was tried, but the strongest reflexion, (020), remained much weaker than the calculated value. The (020) reflexion 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).
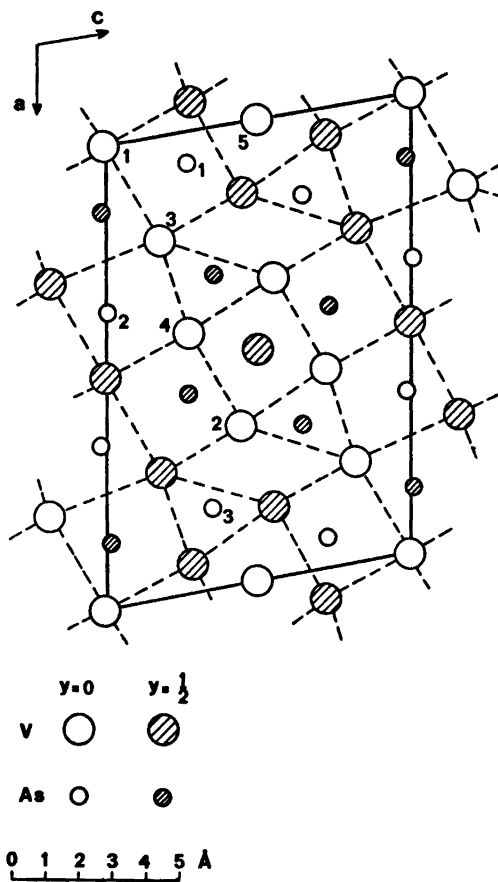

Fig. 1. The crystal structure of β-V$_4$As$_3$ projected on (010).

Table 2. Structure data for β-V$_4$As$_3$, 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, $\beta=100.521(3)°$.

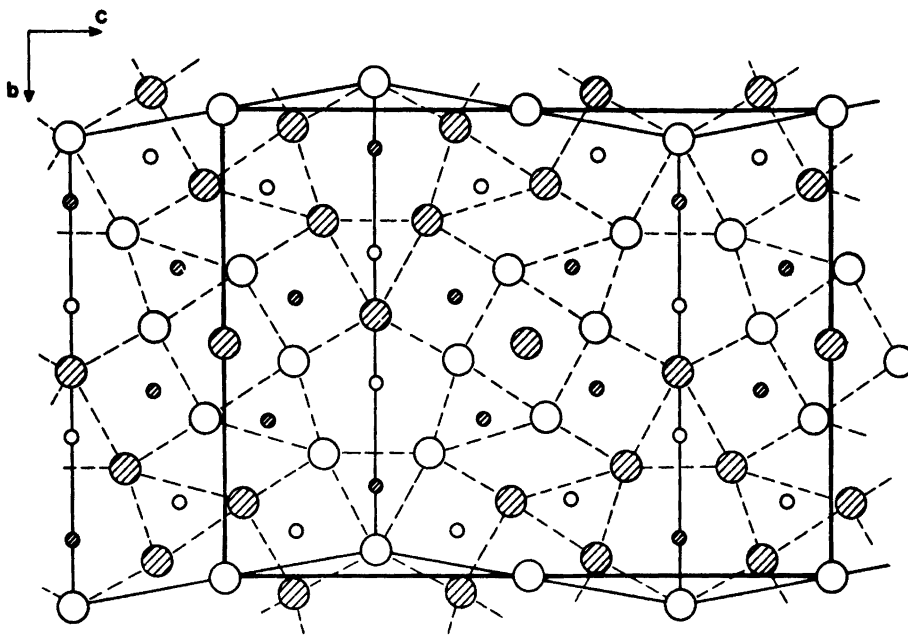| Atom	Position	x	y	z	$\beta_{11} \times 10^5$	$\beta_{22} \times 10^5$	$\beta_{33} \times 10^5$	$\beta_{13} \times 10^5$	$\beta_{12}=\beta_{23}$
V(1)	2a	0	0	0	73(3)	1335(49)	115(6)	9(3)	0
V(2)	4i	0.65796(4)	0	0.44440(5)	68(2)	1220(35)	139(4)	19(2)	0
V(3)	4i	0.22512(4)	0	0.17747(6)	59(2)	1633(38)	279(5)	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. 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 test [11] would probably not be valid, since uncorrected systematic errors are likely to contribute considerably to the differences between F_0 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 Nowotny [7] 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:

$a = 3.4139(2)$ Å; $b = 13.6798(7)$ Å; $c = 18.0598(11)$ Å; $V = 843.4$ Å³.

Thus, the cell-volume of β-V_4As_3 (422.6 Å³) 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 (× 10) for β-V$_4$As$_3$. F_o-values for weak reflexions not included in the refinement are omitted from the table. The columns are h, l, $|F_o|$ and $|F_c|$.

Table 3. Continued.

H,3,L

H,4,L

H,5,L

H,6,L

Table 4. Interatomic distances and standard deviations for β-V$_4$As$_3$ (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 Nb$_4$As$_3$.[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-V$_4$As$_3$ 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-V$_4$As$_3$ 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 Mo$_4$P$_3$[13] is closely related to that of β-V$_4$As$_3$ 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-V$_4$As$_3$, although of the same stoichiometry.

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