

The Crystal Structures of β - V_5As_3 , γ - V_5As_3 and Cr_5As_3

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The crystal structures of two V_5As_3 modifications and Cr_5As_3 have been determined using single-crystal methods (β - V_5As_3) or powder methods (γ - V_5As_3 and Cr_5As_3). The symmetry is orthorhombic (space group $Pnma$). β - V_5As_3 is isotypic with Y_4Bi_3 and has a range of homogeneity. The cell dimensions for a crystal of composition $V_{4.94}As_3$ are $a=6.440$ Å, $b=7.677$ Å, $c=9.285$ Å. γ - V_5As_3 and Cr_5As_3 are isotypic with β - Yb_5Sb_3 . The cell dimensions for γ - V_5As_3 are $a=9.464$ Å, $b=7.520$ Å, $c=6.471$ Å, and for Cr_5As_3 : $a=9.266$ Å, $b=7.449$ Å, $c=6.396$ Å. The two structure types are very similar and are closely related to Rh_5Ge_3 .

The occurrence of a phase of the W_5Si_3 structure type in the V—As system was reported by Boller and Nowotny.¹ They observed^{1,2} that the composition of this phase deviated appreciably from the ideal crystallographic formula. In the following text, this phase is denoted by α - V_5As_3 .

The formation at high temperatures of two additional phases of compositions approximating V_5As_3 was mentioned in an earlier communication.³ A complete crystal-structure analysis of one of them, denoted by β - V_5As_3 (previously³ by β), is reported in the present paper. β - V_5As_3 has the ideal crystallographic formula V_5As_3 , but a moderate range of homogeneity is indicated. The second phase, denoted by γ - V_5As_3 (previously³ by γ), has been found only in arc-melted alloys. X-Ray powder and single-crystal data show that γ - V_5As_3 is isotypic with β - Yb_5Sb_3 .⁴ A β - Yb_5Sb_3 phase has also been found in the Cr—As system.

EXPERIMENTAL

Preparation of β - V_5As_3 . The single crystal of β - V_5As_3 used for collecting the X-ray inten-

sity data was selected from a sample prepared in the following manner.

Vanadium turnings (Vanadium Corp. of America, purity 99.5 %) and arsenic (Koch-Light Laboratories Ltd., claimed purity 99.99 %) were reacted in a silica tube at 900 °C for two days and heated for another four days at 1000 °C. A powder photograph of the sample showed the presence of α - V_5As_3 , β - V_5As_3 and tetragonal V_3As_2 .⁵ Single crystals and crystal aggregates of β - V_5As_3 and V_3As_2 were formed. Normally, crystal formation is slow in this system. Traces of an oxide impurity were also detected, indicating that a chemical vapour-transport reaction involving oxygen-containing molecular species might be responsible for the enhanced crystal growth.

Preparation of γ - V_5As_3 and Cr_5As_3 . Since there is an unavoidable loss of arsenic on arc-melting, both these compounds were synthesized by arc-melting material richer in arsenic than that corresponding to the stoichiometric formulae. The chromium used for the syntheses was labelled as Elektrolyt-Reinstchrom manufactured by Gesellschaft für Elektrometallurgie m.b.H., Nürnberg. A single-phase specimen of γ - V_5As_3 could be obtained but in other samples this phase occurred together with β - V_5As_3 ,⁶ β - V_5As_3 or α - V_5As_3 . Since the solidification process occurs under a very large temperature gradient, these phase-analytical observations cannot serve as any reliable evidence for the phase relationships under equilibrium conditions.

In the arc-melted Cr—As samples, Cr_5As_3 occurred together with CrAs. Heat treatment in a silica tube at 1000 °C for three days yielded CrAs and Cr_4As_3 . No well-formed single crystals could be obtained.

X-Ray powder investigations. The cell dimensions were determined using a Guinier-Hägg type focussing camera with strictly monochromatic $CrK\alpha_1$ radiation [$\lambda=2.28975$ Å] and with silicon ($a=5.431065$ Å)⁶ or germanium ($a=5.657906$ Å)⁷ as internal calibration standards. Cell parameters were refined by the least-squares method. The powder photograph of β - V_5As_3 was indexed using approximate cell dimensions from Weissenberg and oscillation

Table 1. Powder diffraction data for β -V_{4.94}As₃. Cell dimensions: $a = 6.4402(3)$ Å, $b = 7.6767(4)$ Å, $c = 9.2846(5)$ Å.

hkl	$Q \times 10^5$ (Å ⁻²)		Intensity obs. calc.	hkl	$Q \times 10^5$ (Å ⁻²)		Intensity obs. calc.
	obs.	calc.			obs.	calc.	
011	2858	2857	- 0	301	22857	22859	- 7
101	3566	3571	- 1	311	24552	24556	27 27
002		4640	- 0	230	24919	24916	- 9
111	5265	5268	- 2	024	25344	25348	23 33
020	6787	6787	- 0	033	25711	25712	4 13
102		7051	- 0	231		26076	1 1
112	8743	8748	2 2	302	26339	26339	18 12
200	9640	9644	9 3	223	26879	26872	6 6
121	10352	10359	32 20	040	27156	27150	46 54
201	10802	10804	18 9	124	27762	27759	4 5
210	11338	11341	- 2	312	28052	28036	- 3
022	11425	11428	16 5	133	28121	28123	- 5
013	12135	12137	3 2	204		28205	- 0
211		12501	- 0	232		29556	- 0
103	12845	12851	39 23	321	29646	29647	- 4
122	13852	13839	- 0	214		29902	- 0
202	14286	14284	2 1	015		30698	5 5
113		14548	- 0	141	30713	30721	1 1
212		15981	- 1	105	31420	31417	6 7
220		16435	6 6	042	31795	31790	- 1
031	16431	16432	6 0	303	32151	32140	- 1
221	17591	17592	57 62	115		33109	60 3
004	18556	18561	- 5	322	33138	33127	56
131	18844	18843	20 24	313	33844	33837	- 5
123	19638	19639	47 48	142	34207	34201	- 3
203	20082	20085	10 13	224	35002	34992	- 4
104	20977	20972	49 46	233	35366	35356	- 0
222	21079	21072	90 100	134	36243	36244	15 ^a 17
213	21780	21781	17 19	240	36786	36794	3 11
132		22323	- 1	241		37954	- 5
114	22669	22669	4 5	331		38131	- 3

a) Overlapped by Ge b) Overlapped by Si c) Overlapped by α -V₅As₃

photographs. The powder photographs of γ -V₅As₃ and Cr₅As₃ were successfully indexed by comparison with β -V₅As₃, since the cell dimensions are very nearly equal despite structural differences. Powder intensity data were measured densitometrically with a SAAB film scanner using a method similar to that described by Malmros and Werner.⁸ The intensity values obtained were slightly inaccurate due to difficulties in avoiding preferred orientation in the powder samples. Powder diffraction data are given in Table 1 (β -V₅As₃), Table 2 (γ -V₅As₃) and Table 3 (Cr₅As₃).

Single-crystal diffractometry. A many-faceted and well-shaped crystal of β -V₅As₃, with approximate dimensions $0.135 \times 0.098 \times 0.076$ mm, was selected for collecting the intensity data. These were recorded on a computer controlled Stoe-Philips four-circle diffractometer using graphite monochromatized MoK α radiation. A step-scan procedure was used for recording the reflexions to a maximum in 2θ of 89° . The part of reciprocal space covered was limited by $-12 \leq h \leq 12$, $0 \leq k \leq 14$ and $-16 \leq l \leq 18$. Instrumental stability and crystal setting were checked regularly using three standard reflexions remeasured every 50 reflexions. The strongest of these three, (040), was found to vary somewhat erratically, while the other two remained within expected fluctuations.

Calculations. The calculations were performed on IBM 370/155 and IBM 1800 computers. The crystallographic programs are listed in Ref. 9. The LINNE film scanner program is a modification of the PILT program devised by G. Malm-

ros.⁸ Absorption corrections, with an approximate description of the crystal using 14 limiting faces, were applied to the single-crystal data. The minimum and maximum transmission factors were 0.0891 and 0.1775, using a calculated linear absorption coefficient of 329 cm^{-1} .

DETERMINATION OF THE β -V₅As₃ STRUCTURE

The data obtained from Weissenberg films indicated orthorhombic symmetry, with systematic absences corresponding to the space groups $Pnma$ or $Pn2_1a$. The symmetry and the cell volume together with phase-analytical data suggested a unit-cell content of 20 vanadium and 12 arsenic atoms.

In the preliminary structure analysis, the Harker sections $P(u,0,w)$, $P(u,\frac{1}{2},w)$ and $P(u,v,\frac{1}{2})$ of the Patterson function were calculated, the intensity material being uncorrected for absorption and averaged intensity values being used for sets of reflexions that should be equivalent according to the orthorhombic symmetry.

The interpretation of the Patterson function was facilitated by the following considerations. The very strong (040) reflexion indicated that the atoms must be essentially confined to planes approximately $b/4$ apart. Moreover, the very weak (020) reflexion indicated that these planes scatter approximately equally. These observations, together with the fact that the scattering power of an arsenic atom is roughly twice that of vanadium, led to the assumption that vanadium and arsenic occupy one $8d$ position each, with $y \sim 0$, and the rest of the atoms are distributed in $4c$ positions in the space group $Pnma$.

The coordinates from the Harker sections, together with distance considerations, gave a reasonable model of the structure. F_o -syntheses were made and the positional parameters found, together with one scale-factor and six individual isotropic temperature factors, were refined using a full-matrix least-squares method. The atomic scattering factors were taken from Ref. 10 and the dispersion correction factors from Ref. 11. After four cycles a conventional R -value of 0.046 was obtained based on the 1538 strongest reflexions. Now that the assumed composition was confirmed, a linear absorption coefficient was calculated,

Table 2. Powder diffraction data for γ -V₅As₃. Cell dimensions: $a = 9.4640(3)$ Å, $b = 7.5204(2)$ Å, $c = 6.4712(2)$ Å.

hkl	$Q \times 10^5$ (Å ⁻²)		Intensity		hkl	$Q \times 10^5$ (Å ⁻²)		Intensity	
	obs.	calc.	obs.	calc.		obs.	calc.	obs.	calc.
101	3505	3504	-	1	231	22771	22767	-	9
011	4156	4156	-	3	013	23254	23260	-	6
200	4466	4466	-	0	113	24376	24376	-	0
111	5273	-	0	420	24935	24936	61	66	
210	6234	-	1	203	25962	25958	35	20	
201	6854	-	0	132	26588	26582	2	6	
020	7073	7073	-	0	322	26675	26673	-	4
211	8622	8622	6	4	421	27324	27324	10	7
002	9553	9552	-	5	402	27416	-	1	
121	10577	10577	43	20	213	27723	27726	35	35
102	10666	10668	15	6	040	28292	28290	50	70
220	11537	11538	20	8	331	28350	-	3	
301	12438	12436	66	32	412	29184	-	1	
112	12438	12436	66	32	123	29681	-	2	
221	13926	-	4	232	29931	29931	-	6	
202	14012	14018	-	1	501	30300	30300	-	3
311	14204	-	1	303	31540	-	1		
212	15791	15786	-	3	141	31795	-	2	
022	16624	-	0	511	32068	32068	-	3	
122	17743	17741	108	95	240	32756	-	0	
400	17869	17864	-	6	223	33028	33030	34	45
031	18303	18301	7	21	313	33308	-	1	
131	19427	19418	6	9	430	33773	33777	5	10
321	19506	19509	49	50	422	34489	34488	6	8
302	19606	19600	16	23	241	35134	35144	-	2
410	19632	-	14	332	35510	35513	23	15	
401	20249	20252	14	48	431	36156	36165	-	2
230	20380	20379	-	2	521	37372	-	41	
222	21092	21090	86	100	033	37379	37405	66	6
312	21365	21368	14	4	502	37464	-	3	
411	22018	22020	3	9	042	37832	37842	8	9
103	22611	22608	9	20					

*) Atomic coordinates taken from β -Yb₅Sb₃

Table 3. Powder diffraction data for Cr₅As₃. Cell dimensions: $a = 9.2655(4)$ Å, $b = 7.4493(3)$ Å, $c = 6.3959(2)$ Å.

hkl	$Q \times 10^5$ (Å ⁻²)		Intensity		hkl	$Q \times 10^5$ (Å ⁻²)		Intensity	
	obs.	calc.	obs.	calc.		obs.	calc.	obs.	calc.
101	3615	3609	2	1	411	ε	22884	-	9
011	4245	4247	-	3	103	23168	23166	23	21
200	4659	-	0	0	231	23322	-	9	
111	5411	-	0	013	23801	23803	5	6	
210	6441	-	1	113	24968	-	0		
201	7104	-	0	420	25847	25846	62	66	
020	7208	-	0	203	26660	26660	33	19	
211	8911	8906	4	4	132	27166 ^a	27161	4	6
002	9779	9778	4	4	322	27487	27470	-	4
121	10814	10818	28	16	421	28290	28290	19	7
102	10947 ^a	10943	-	5	402	28416	-	1	
220	11865	11868	15	5	213	28459	28462	51	34
112	12744	12745	3	2	040	28835	28833	56	70
301	12926	12928	45	27	331	29147	-	3	
221	14301	14312	-	6	412	30218	-	1	
202	14437	-	3	123	30374	-	2		
311	14730	-	1	232	30657	30656	-	6	
212	16239	-	2	501	31566	-	3		
022	16986	-	0	141	32442	-	1		
122	18147	18151	85	94	303	32484	-	2	
400	18637	-	6	511	33368	-	2		
031	18662	18663	39	21	240	33492	-	0	
131	19829	19828	11	7	223	33878	33868	33	44
321	20137	20136	39	50	313	34286 ^b	34286	-	1
302	20257	20262	11	24	430	34854	34856	-	10
410	20443	20439	12	1	422	ε	35624	-	7
230	ε	20878	-	2	241	ε	35937	-	7
401	21086	21082	29	48	332	36479	36480	30	15
222	21447	21446	92	100	431	37308	37300	3	2
312	22059	22064	10	3					

*) Atomic coordinates taken from β -Yb₅Sb₃

a) Overlapped by Si b) Overlapped by Ge c) Overlapped by CrAs

and an absorption correction applied. In order to correct for extinction effects only reflexions having identical indices were averaged.

A series of least-squares refinements was started. The function minimized was

$$w(|F_o| - |F_c|)^2, \text{ where } w^{-1} = \sigma^2 + (p|F_o|)^2$$

σ is the standard deviation of F_o , based on counting statistics, and $p = 0.01$ is an empirical factor. Eleven reflexions were excluded due to obviously misread data, and the (040) reflexion was excluded because it behaved inconsistently during measurement and because it was probably strongly influenced by extinction effects. Reflexions with 'negative intensities' were omitted. An extinction correction according to Coppens and Hamilton,¹² based on approximations introduced by Zachariasen, was applied to the rest of the material. The isotropic temperature factors of two vanadium atoms were found to be somewhat larger than expected; the occupancy factors of these two positions were allowed to vary as the observation of cell parameter variations had indicated the probability of structure defects. Finally, anisotropic temperature factors were introduced. After convergence, the following discrepancy indices were obtained (3547 reflexions):

$$R(F) = 0.035, \text{ where } R(F) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

and

$$R_w(F) = 0.035, \text{ where } R_w(F) = \frac{[\sum w(|F_o| - |F_c|)^2]^{1/2}}{\sum w|F_o|^2}$$

In line with the suggestion of Hirshfeld and Rabinovich¹³ a final refinement was made based on F^2 rather than on F , including reflexions with 'negative intensities' to preserve the assumed normal distribution in the intensity data. For the 3645 reflexions refined the following R -values were obtained, $R(F^2) = 0.038$ and $R_w(F^2) = 0.059$, defined in a similar manner as above, only that F^2 replaces F in the formulae. The corresponding $R(F)$ was 0.034. No significant change in parameter values was found, but the standard deviations were somewhat lower than for the F refinement.

At this stage it was felt, that because of expected strong correlations between many of the parameters, any further refinement assuming the non-centrosymmetric $Pn2_1a$ symmetry would not be worthwhile. The very close agreement between the observed and

Table 4. Structure data for β -V₄As₃, including anisotropic thermal parameters β_{ij} ($\times 10^3$). The form of the temperature factor is $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 + 2\beta_{12}hk + \dots)$. Standard deviations within brackets.

Atom	Position	Occupancy (%)	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
V(1)	8d	100	0.20848(4)	0.55282(4)	0.06395(3)	243(4)	230(3)	159(2)	21(3)	-21(2)	11(2)
V(2)	4c	99.1(2)	0.14603(6)	1/4	0.78443(4)	364(7)	303(5)	158(3)	0	-33(4)	0
V(3)	4c	94.6(2)	0.28572(7)	1/4	0.26722(4)	333(7)	365(6)	142(4)	0	-46(4)	0
V(4)	4c	100	0.45513(6)	1/4	0.01131(4)	275(6)	193(4)	127(3)	0	-14(3)	0
As(1)	8d	100	0.07048(2)	0.50822(2)	0.32661(2)	290(3)	229(2)	126(1)	-25(2)	13(1)	-1(1)
As(2)	4c	100	0.05788(4)	1/4	0.04406(3)	248(4)	219(3)	148(2)	0	-28(2)	0

calculated structure factors implies that any deviation from centrosymmetry must be negligibly small, and the final structure is accordingly described in the terms of *Pnma* symmetry as presented in Table 4 (with parameter values taken from the F^2 refinement). A list of observed and calculated structure factors can be obtained from the author on request.

THE STRUCTURES OF γ -V₅As₃ AND Cr₅As₃

When the β -V₅As₃ structure had been determined it was seen to resemble closely the β -Yb₅Sb₃ structure,⁴ the two compounds nevertheless representing different structure types. It appeared, however, that β -Yb₅Sb₃ might be truly isotypic with γ -V₅As₃ and Cr₅As₃. Powder intensity calculations were accordingly performed for the two arsenides, assuming this isotypism and using the atomic coordinates of β -Yb₅Sb₃, as given by Brunton and Steinfink.⁴ A satisfactory agreement was found between observed and calculated intensities for both arsenides as presented in Tables 2 and 3, leaving no doubt that the three compounds are isostructural.

STRUCTURAL DESCRIPTIONS AND DISCUSSION

A projection of the β -V₅As₃ structure along the *b*-axis is illustrated in Fig. 1a. The coordination around As(1) may be characterized by a trigonal prismatic arrangement of metal atoms with three further atoms outside the prism faces. A closer look at the distances reveals that the trigonal prism is indeed very distorted; from this point of view the coordination is characterized better by the coordination number 8. The coordination polyhedron around As(2) is much more regular, a bisdisphenoidal arrangement with coordination number 8. Interatomic distances are presented in Table 5. The distances between unlike atoms in β -V₅As₃ are similar to those found in α -V₄As₃¹⁴ and β -V₄As₃.⁵ The V(3)–V(4) distance of 2.61 Å is rather short, but the V(3) site is not fully occupied. Still shorter metal contacts are found in α -V₄As₃ (2.40 Å) and V₅As (2.38 Å).¹⁵ In these two arsenides the metal atoms form straight infinite chains, but there are no data, as to the occupancy in these phases albeit cell parameter

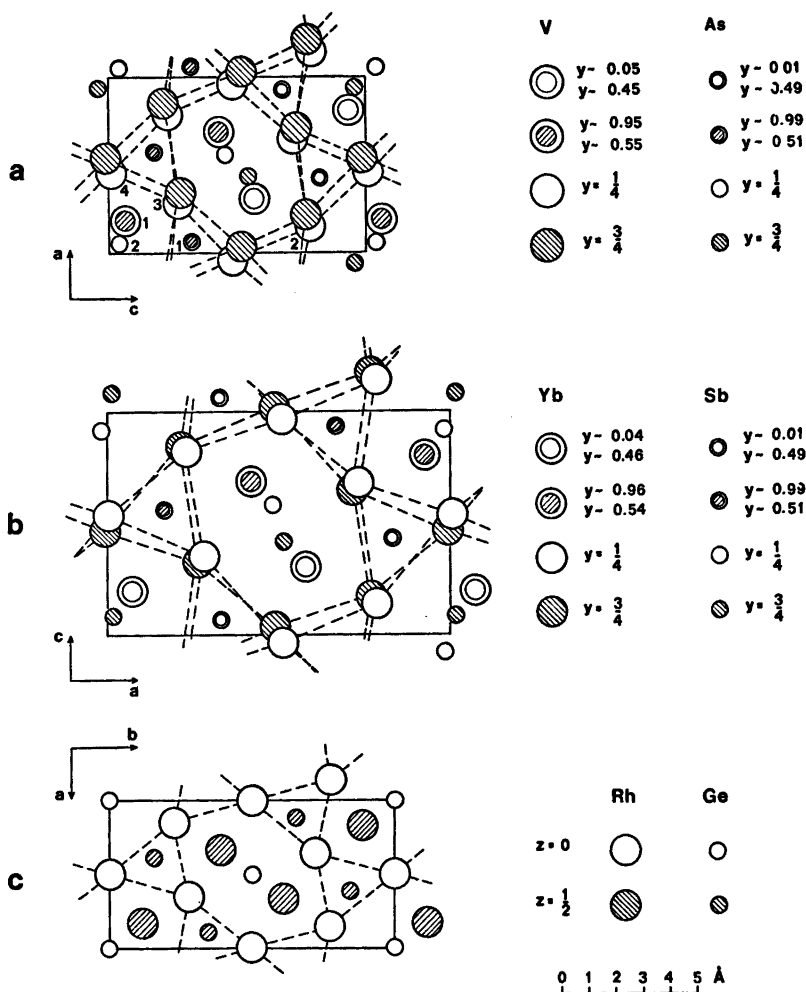


Fig. 1. The crystal structures of (a) β -V₅As₃ and (b) β -Yb₅Sb₃, projected along the b-axes, and (c) Rh₅Ge₃ projected along the c-axis.

variations indicate the possibility of vacancies in both.

There is a striking resemblance between the β -V₅As₃ structure and the β -Yb₅Sb₃ structure, the latter being illustrated in Fig. 1b. There is also a close relationship to the Rh₅Ge₃ structure¹⁶ illustrated in Fig. 1c; this fact was already recognized by Brunton and Steinfink in the case of β -Yb₅Sb₃. Owing to the lack of positional parameter data for γ -V₅As₃, no closer comparison can be made as regards distances and coordination in the orthorhombic V₅As₃ polymorphs.

Cell dimension variations⁸ of β -V₅As₃ indicated a homogeneity range. In quenched specimens the cell volume was smaller, which could be interpreted as an increasing tendency to vacancy formation at higher temperatures. The a and b axes decrease and the c axis increases with decreasing volume. The structure refinement supported this view, indicating vanadium deficiency, the composition of the investigated crystal being V_{4.94}As₃.

β -V₅As₃ is most probably isotypic with Y₅Bi₃, reported by Schmidt *et al.*,¹⁷ as well as with a further number of rare-earth bismuthides

Table 5. Interatomic distances (Å) for β - $V_{4.94}As_3$. The maximum standard deviation obtained was 0.0006 Å. Distances shorter than 3.5 Å are listed.

V(1)–As(8)	2.492	V(4)–2 As(1)	2.532	
As(2)	2.526	As(2)	2.576	
As(1)	2.566	2 As(1)	2.597	
As(1)	2.665	V(3)	2.615	
As(1)	2.618	2 V(1)	2.734	
V(2)	2.713	2 V(1)	2.858	
V(4)	2.734	V(2)	2.898	
V(4)	2.858	V(3)	2.960	
V(1)	3.027	V(2)	3.009	
V(3)	3.035	As(1)–	V(3)	2.481
V(1)	3.046	V(4)	2.532	
V(2)	3.080	V(2)	2.540	
V(3)	3.144	V(1)	2.566	
		V(4)	2.597	
V(2)–As(2)	2.477	V(1)	2.618	
2 As(1)	2.540	V(2)	2.633	
2 As(1)	2.633	V(1)	2.665	
2 V(1)	2.713	V(3)	2.838	
V(4)	2.898	As(2)	3.289	
V(4)	3.009	As(1)	3.348	
2 V(1)	3.080			
2 V(2)	3.283	As(2)–	V(2)	2.477
		V(3)	2.478	
V(3)–As(2)	2.478	2 V(1)	2.498	
2 As(1)	2.481	2 V(1)	2.526	
As(2)	2.539	V(3)	2.539	
V(4)	2.615	V(4)	2.576	
2 As(1)	2.838	2 As(1)	3.289	
V(4)	2.960			
2 V(1)	3.035			
2 V(1)	3.144			
2 V(3)	3.236			

recently reported by Yoshihara *et al.*¹⁸ Schmidt *et al.* gave the composition of 37.8 at.% Bi (corresponding to the formula $Y_{4.94}Bi_3$) for a homogeneous single phase sample. This indicates that analogous metal vacancy distributions might occur in β - V_4As_3 and Y_5Bi_3 . Yoshihara *et al.*, however, assign the formula $R_{5+z}Bi_3$ to their compounds, indicating deviations from the ideal composition towards the metal-rich side.

No range of homogeneity was detectable for γ - V_5As_3 . This corresponds to the results for the isostructural β - Yb_5Sb_3 , which was found to be strictly stoichiometric.⁴

The small amounts of homogeneous material available did not permit a conventional chemical analysis. An attempt to perform microprobe analyses on the very crystal examined

and on γ - V_5As_3 failed to detect any significant deviations from the stoichiometric composition. The relative error of a microprobe analysis is of the same magnitude as the proposed deviation in composition.

α - V_5As_3 appears to form narrow two-phase regions with β - and γ - V_5As_3 , with α - V_5As_3 as the most metal-rich component. Its cell volume is considerably smaller than that of the orthorhombic phases and has been found to vary, indicating non-stoichiometry. The variations affect the *c*-axis to the greatest extent. It is therefore likely that a vacancy mechanism involving a variable occupancy of the 4*a* or 4*b* positions (space group *I4/mcm*) is responsible for this behaviour. A complete single-crystal analysis has been started in order to study this problem. The results will be presented in a forthcoming paper.

In comparing the V–As and Cr–As systems it is notable that, when vanadium arsenide polymorphs exist, only the structure types adopted by the high-temperature phases are represented in the Cr–As system. This is illustrated by the couples Cr_4As_3 – β - V_4As_3 (Cr_4As_3 type) and Cr_5As_3 – γ - V_5As_3 (β - Yb_5Sb_3 type).

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