

# The Crystal Structure of $V_3As_2$

ROLF BERGER

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

The crystal structure of  $V_3As_2$  has been determined by means of single-crystal diffractometry. The symmetry is tetragonal, space group  $P4/m$ , and lattice parameters  $a=9.4128$  Å and  $c=3.3361$  Å. The structure constitutes a new structure type related to the  $Ti_3Te_4$  type.

Boller and Nowotny<sup>1</sup> assigned the composition  $V_3As_2$  to a phase that was later<sup>2</sup> proved to be  $V_4As_3$  (orthorhombic), and they also indicated the presence of further phases in this composition range.<sup>3</sup> Since they gave no powder data, it is unclear whether their preparations contained  $V_3As_2$  (*vide infra*) or even  $\beta$ - $V_4As_3$ <sup>4</sup> or  $\beta$ - $V_5As_3$ .<sup>5</sup> This paper presents a complete single-crystal X-ray determination of the structure of  $V_3As_2$ , showing that the proposed composition and the space-group assignment given earlier<sup>4</sup> are correct.

## EXPERIMENTAL

**Preparation.**  $V_3As_2$  forms readily in silica-tube syntheses and decomposes at higher temperatures. The formation of  $V_3As_2$  crystal aggregates, together with  $\beta$ - $V_5As_3$ , was reported earlier.<sup>5</sup> The crystals, probably formed by a vapour transport process, were severely intergrown, making it difficult to find a single crystal.

**Single-crystal diffractometry.** A small needle-shaped crystal was selected for the intensity data collection. Its dimensions were  $10 \times 12 \times 80$   $\mu$ m and it was limited by  $\{110\}$  and  $\{001\}$  faces. The equipment and intensity-collecting procedure is described elsewhere.<sup>4,5</sup> The part of the reciprocal space covered was limited by  $-13 \leq h \leq 13$ ,  $-13 \leq k \leq 13$  and  $0 \leq l \leq 4$ , corresponding to a maximum in  $2\theta$  of  $60^\circ$ . The instrumental and crystal setting stability was checked by remeasuring three reflexions at regular intervals throughout the data collection period. This procedure revealed no drift.

**X-Ray powder investigations.** The lattice dimensions were determined on powdered crystals using a Guinier-Hägg focussing camera equipped with  $CuK\alpha_1$  radiation. Germanium ( $a=5.657906$  Å) was added as an internal calibration standard, and the unit cell dimensions were refined by the method of least squares. Powder intensities were measured densitometrically using a SAAB Mark II film scanner. The powder data, presented for identification purposes, are collected in Table 1.

**Numerical calculations.** All calculations were performed on IBM 1800 and IBM 370/155 computers using local crystallographic programs.<sup>6</sup> The calculations included an absorption correction (Gaussian grid) yielding the minimum and maximum transmission factors 0.67 and 0.74 for a linear absorption coefficient of  $308$   $cm^{-1}$ .

## STRUCTURE DETERMINATION

The preliminary Weissenberg and oscillation photographs revealed a primitive tetragonal cell, without any systematic absences among the reflexions. However, the Laue symmetry was either  $4/m$  or  $4/mmm$  for different crystals. This indicated that some crystals were in fact ideal twins showing false mirror planes, and that the true point group ought to be  $4/m$ . Unfortunately, this also implied that the absence of a  $(110)$  mirrorplane did not exclude the presence of at least some twin character. In fact, one early attempt to solve the structure failed because the data were marred by this effect. In order to avoid twinning, a smaller crystal was eventually selected, which did indeed show a more marked difference between the  $(hkl)$  and  $(khl)$  reflexions than any of the previously investigated crystals. The most probable space group was  $P4/m$  (No. 83), with the atoms situated at  $z=0$  and  $z=\frac{1}{2}$ , which was supported by the short axis and the

Table 1. Powder diffraction data (CrK $\alpha_1$  radiation) for V<sub>3</sub>As<sub>2</sub>. Indices (*hkl*) denote both (*hkl*) and (*hkl*) reflexions. Cell dimensions: *a* = 9.4128(3) Å, *c* = 3.3361(2) Å.

<u>hkl</u>	Q $\times 10^5$ (Å <sup>-2</sup> )		Intensity		<u>hkl</u>	Q $\times 10^5$ (Å <sup>-2</sup> )		Intensity	
	obs.	calc.	obs.	calc.		obs.	calc.	obs.	calc.
100		1129	-	0	311	20263	20272	50{	32
110		2257	-	0	330	20313	20316		13
200	4510	4515	3	1	420	22579	22573	69	75
210	5637	5643	2	1	321	23661	23658	46	44
001		8985		1	401	27058	27044	4	4
220	9025	9029	35{	25	411	28173	28172		96
101	10111	10114		16	430		28217	102{	12
300	10159	10158	35{	7	500				1
111		11242	-	0	331	29337	29301	13{	4
310	11288	11287	31	26	510		29345		8
201		13500	-	0	421	31551	31558	25	24
211	14620	14628		100	520	32727	32731	33	33
320		14673	103{	3	002	35945	35941	67	67
221	18011	18014		19	440		36117	-	0
400	18063	18059	40{	15	102		37069	-	0
301	19144	19143		80	431				38
410		19187	80{	5	501	37193	37202	47{	10

similar intensity distribution of the *l* = 0 and *l* = 2 zones.

The Patterson sections  $P(uv0)$  and  $P(uv\frac{1}{2})$  were thus calculated, and a reasonable structure model was derived, consistent with 12 vanadium and 8 arsenic atoms to the cell. The approximate composition was deduced by considering the average atomic volume compared with those of the neighbouring phases. The approximate positional parameters were refined from Fourier syntheses, and eventually a series of full-matrix least-squares refinements was started, based on  $F$  in the preliminary stages and finally on  $F^2$  to include reflexions with "negative intensity" values.<sup>7,8</sup> The atomic scattering factors and dispersion corrections were taken from Ref. 9 and 10, respectively.

The first refinement on an averaged reflexion material with one scale factor, seven isotropic thermal parameters and eight positional parameters converged to  $R(F) = 0.031$ , the very weakest reflexions being given zero weight (378 reflexions). The introduction of anisotropic thermal parameters gave the residual index  $R(F) = 0.023$ . The strongest reflexions were systematically weaker than calculated, and therefore an extinction correction according to Coppens and Hamilton<sup>11</sup> was performed, neglecting effects of primary beam shape.<sup>12</sup> Since the same extinction occurs only for Friedel-related reflexions, averaging between equivalent non-identical reflexions was no longer permissible. Thirteen reflexions were excluded from the final refinement on  $F^2$ ,

Table 2. Structure data for V<sub>3</sub>As<sub>2</sub>, including anisotropic thermal parameters  $U_{ij}$  ( $\times 10^4$ ) Å<sup>2</sup>. The form of the temperature factor is  $\exp[-2\pi(U_{11}h^2 + U_{22}k^2 + 2U_{12}hk)\alpha^{*2} - 2\pi U_{33}l^2c^{*2}]$ ;  $U_{13} = U_{23} = 0$ . Standard deviations in parentheses. Space group:  $P4/m$  (No. 83).

Atom	Position	<i>x</i>	<i>y</i>	<i>z</i>	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$
V(1)	4 <i>k</i>	.13335(9)	.17927(9)	$\frac{1}{2}$	72(4)	53(4)	80(4)	-0(3)
V(2)	4 <i>j</i>	.39694(9)	.28477(9)	0	61(4)	70(4)	66(5)	3(3)
V(3)	2 <i>f</i>	0	$\frac{1}{2}$	$\frac{1}{2}$	76(6)	99(6)	128(7)	26(4)
V(4)	1 <i>d</i>	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	40(4)	$U_{11}$	102(9)	0
V(5)	1 <i>a</i>	0	0	0	53(5)	$U_{11}$	103(9)	0
As(1)	4 <i>k</i>	.24604(5)	.41181(5)	$\frac{1}{2}$	54(2)	54(2)	62(3)	-2(2)
As(2)	4 <i>j</i>	.28481(5)	.03946(5)	0	64(2)	58(2)	60(2)	-2(2)

which yielded  $R(F^2)=0.056$  and  $R_w(F^2)=0.064$ , with the corresponding  $R(F)=0.055$  (1834 refl.). The agreement factors are defined below:

$$R(F^n) = \frac{\sum ||F_o^n| - |F_c^n||}{\sum |F_o^n|}$$

$$R_w(F^n) = \left[ \frac{\sum w(|F_o^n| - |F_c^n|)^2}{\sum w|F_o^n|^2} \right]^{1/2} \quad n=1,2$$

Here,  $w^{-1} = \sigma_c^2 + (p_n|F_o^n|)^2$ , where  $\sigma_c$  is the standard deviation of  $F_o^n$  based on counting statistics, and  $p_n$  ( $p_2=0.02$ ) is an empirical factor to allow for instrumental errors.

Superficially there does not seem to be any gain in the final refining model when comparing the  $R$ -values from the different series. However, the very low  $R(F)=0.023$  relates to a reduced reflexion material, and intensity thresholds affect the  $R$ -value considerably while  $R_w$  is less sensitive.<sup>7,13</sup> As regards the parameters, the result is not significantly different between refinements made on averaged or unaveraged material, but only the latter can be used for the appropriate extinction correction. For the crystal used in this determination, the mean path lengths for X-rays corresponding to equivalent reflexions are approximately the same and would lead to similar extinction corrections within an equivalent set. For comparison only, an extinction correction was performed on an averaged reflexion material. This refinement gave an  $R(F^2)$ -value of 0.030 (495 refl.), considerably lower than 0.056 (1834 refl.). This might indicate that the whole material suffers from some twin character of the crystal, the effects of which are reduced in the averaging process. However, a  $\Delta R$  normal probability plot<sup>14</sup> for the unaveraged material had a slope of 0.97 and an intercept of  $-0.03$ , indicating a fairly random error distribution and appropriate individual weights.

The structure data based on the final  $F^2$  refinement are given in Table 2, while the structure factors can be obtained on request from the author.

## DISCUSSION OF THE STRUCTURE

The structure of  $V_3As_2$  constitutes a new structure type. A projection of the structure is shown in Fig. 1b. Its typical features are the metal b.c.c. units and the trigonal prismatic arrangements, both common structural

elements also in  $\alpha$ - $V_4As_3$ <sup>2</sup> and  $\beta$ - $V_4As_3$ <sup>4</sup> as well as in other transition metal compounds with phosphorus and arsenic.

The structure of  $V_3As_2$  can be regarded as a "filled"  $Ti_5Te_4$  structure,<sup>15</sup> the latter being

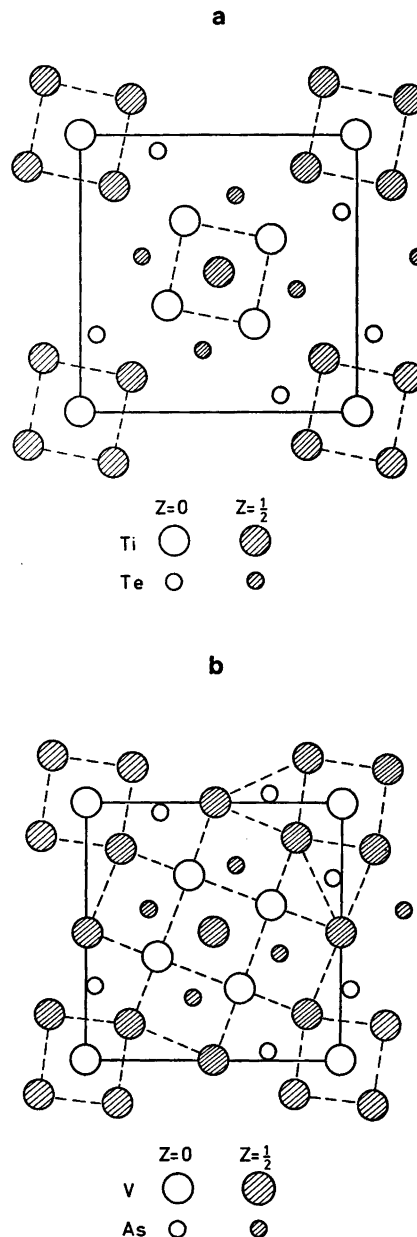


Fig. 1. The structures of (a)  $Ti_5Te_4$  and (b)  $V_3As_2$  projected on (001).

Table 3. Interatomic distances (Å) and coordination in  $V_3As_2$ . Distances shorter than 3.5 Å are listed. Standard deviations in parentheses.

V(1) — As(1)	2.432(1)	V(4) — 4As(1)	2.531(0)
— 2As(2)	2.533(1)	— 8V(2)	2.798(1)
— 2As(2)	2.559(1)	— 2V(4)	3.336(0)
— 2V(5)	2.684(1)		
— 2V(1)	2.974(1)	V(5) — 8V(1)	2.684(1)
— 2V(2)	3.150(1)	— 4As(2)	2.706(0)
— V(3)	3.270(1)	— 2V(5)	3.336(0)
— 2V(1)	3.336(0)		
		As(1) — V(1)	2.432(1)
V(2) — 2As(1)	2.481(1)	— V(3)	2.460(0)
— 2As(1)	2.496(1)	— 2V(2)	2.481(1)
— As(2)	2.539(1)	— 2V(2)	2.496(1)
— 2V(4)	2.798(1)	— V(4)	2.531(0)
— 2V(1)	3.150(1)	— 2As(1)	3.336(0)
— 2V(2)	3.177(1)	— 2As(2)	3.381(1)
— 2V(3)	3.303(1)		
— 2V(2)	3.336(0)	As(2) — 2V(1)	2.533(1)
		— V(2)	2.539(1)
V(3) — 2As(1)	2.460(0)	— 2V(1)	2.559(1)
— 4As(2)	2.650(0)	— 2V(3)	2.650(0)
— 2V(1)	3.270(1)	— V(5)	2.706(0)
— 4V(2)	3.303(1)	— 2As(2)	3.336(0)
— 2V(3)	3.336(0)	— 2As(1)	3.381(1)

depicted in Fig. 1a.  $V_3As_2$  is formally generated by inserting metal atoms in the octahedral voids formed by the non-metal atoms. The symmetry then changes from  $I4/m$  to  $P4/m$ . Among the arsenides, the  $Ti_5Te_4$  structure is adopted by  $Ta_5As_4$ <sup>16</sup> and  $Mo_5As_4$ .<sup>17</sup> In this context it is interesting to note that, during their attempts to refine the  $Mo_5As_4$  structure, Jensen and Kjekshus invariably found the Laue symmetry  $4/mmm$  for their crystals due to twinning.

In view of the relationship between the  $V_3As_2$  and  $Ti_5As_4$  structures, new ternary compounds of the  $V_3As_2$  type, such as  $M_3M'X_4$ , might possibly be formed by filling up binary  $Ti_5Te_4$  structures with small metal atoms. This would lead to an increase in cell dimensions accompanied by a breakdown of the body-centring. The introduction of iron in  $Mo_5As_4$  yields a unit cell decrease consistent with Mo-Fe substitution.

The interatomic distances in  $V_3As_2$  are presented in Table 3. The V-As distances show no great deviations from those found in the other vanadium arsenides. It may be noted that the intermetallic distances within the non-equivalent b.c.c. units differ significantly, possibly owing to different environments around these units. Thus V(5) has eight vana-

dium neighbours at bonding distances, while V(4) is more tightly bound to its four arsenic neighbours. The thermal anisotropy is rather large for V(4), with relatively small components in the  $z = \frac{1}{2}$  plane. This is similar to the situation in  $\beta-V_4As_3$ ,<sup>4</sup> where essentially the same coordination occurs. Here  $U_{11} = 0.0041(2)$ ,  $U_{33} = 0.0035(2)$  and  $U_{13} = 0.0005(2)$ , all being components in the corresponding plane, while the perpendicular component  $U_{22} = 0.0093(3)$ . Consequently, it is likely that the thermal parameters for V(4) as given in Table 2 are essentially correct and not the result of biased data.

The composition  $M_3X_2$  is not common among the transition metal arsenides, the only representatives so far being  $Hf_3As_2$ <sup>18</sup> and  $Zr_3As_2$ ,<sup>19</sup> both of the  $Hf_3P_2$  type.<sup>20</sup> This, and also the  $Cr_3C_2$  structure,<sup>21</sup> are entirely built up of interconnected trigonal prisms, and their anti-types are found among the lanthanide and actinide sulfides.<sup>22-24</sup> Anti-types to the  $V_3As_2$  structure would hardly be found among these compounds because of the occurrence of the b.c.c. elements which have no counterpart among sulfide structures.

*Acknowledgements.* The author thanks Professor I. Olovsson for all the facilities provided and is also grateful to Professor S. Rundqvist

for his helpful comments. This work was financially supported by the Swedish Natural Science Research Council.

## REFERENCES

1. Boller, H. and Nowotny, H. *Monatsh. Chem.* 97 (1966) 1053.
2. Yvon, K. and Boller, H. *Monatsh. Chem.* 103 (1972) 1643.
3. Boller, H. and Nowotny, H. *Monatsh. Chem.* 98 (1967) 2127.
4. Berger, R. *Acta Chem. Scand. A* 28 (1974) 771.
5. Berger, R. *Acta Chem. Scand. A* 30 (1976) 363.
6. Lundgren, J.-O., Ed., *Crystallographic Computer Programs*, Institute of Chemistry, University of Uppsala, Uppsala 1975, UUIC-B13-04-2.
7. Hirshfeld, F. L. and Rabinovich, D. *Acta Crystallogr. A* 29 (1973) 510.
8. Wilson, A. J. C. *Acta Crystallogr. A* 32 (1976) 781.
9. Doyle, P. A. and Turner, P. S. *Acta Crystallogr. A* 24 (1968) 390.
10. Cromer, D. T. and Libermann, D. *J. Chem. Phys.* 53 (1970) 1891.
11. Coppens, P. and Hamilton, W. C. *Acta Crystallogr. A* 26 (1970) 71.
12. Urban, J. P. *Acta Crystallogr. A* 32 (1976) 631.
13. Stenkamp, R. E. and Jensen, L. H. *Acta Crystallogr. B* 31 (1975) 1507.
14. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. IV, p. 293.
15. Grønvold, F., Kjekshus, A. and Raaum, F. *Acta Crystallogr.* 14 (1961) 930.
16. Rundqvist, S., Carlsson, B. and Pontchour, C.-O. *Acta Chem. Scand.* 23 (1969) 2188.
17. Jensen, P. and Kjekshus, A. *Acta Chem. Scand.* 20 (1966) 1309.
18. Rundqvist, S. and Carlsson, B. *Acta Chem. Scand.* 22 (1968) 2395.
19. Carlsson, B., Gölin, M. and Rundqvist, S. *Acta Chem. Scand. A* 30 (1976) 386.
20. Lundström, T. *Acta Chem. Scand.* 22 (1968) 2191.
21. Rundqvist, S. and Runnsjö, G. *Acta Chem. Scand.* 23 (1969) 1191.
22. Sleight, A. W. and Prewitt, C. T. *Inorg. Chem.* 7 (1968) 2282.
23. Range, K.-J. and Leeb, R. *Z. Krist.* 140 (1974) 424.
24. Zachariasen, W. H. *Acta Crystallogr.* 2 (1949) 291.

Received December 1, 1976.