

## Crystal Structure Refinement of $\alpha$ -V<sub>5</sub>As<sub>3</sub>

ROLF BERGER

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

The crystal structure of  $\alpha$ -V<sub>5</sub>As<sub>2.74</sub> has been refined on  $F^2$  to an  $R$ -value of 2.7 % using X-ray single-crystal data. The symmetry is tetragonal, space group  $I4/mcm$ . The compound is arsenic-deficient and is isostructural with W<sub>5</sub>Si<sub>3</sub>. The cell dimensions are:  $a=9.5031(4)$  Å and  $c=4.8255(3)$  Å.

The V—As system contains three phases of composition approximating to V<sub>5</sub>As<sub>3</sub>. Two of these,  $\beta$ -V<sub>5</sub>As<sub>3</sub> and  $\gamma$ -V<sub>5</sub>As<sub>3</sub>, are stable only at elevated temperatures,<sup>1</sup> while  $\alpha$ -V<sub>5</sub>As<sub>3</sub> also forms in silica-tube syntheses. The latter phase was first reported by Boller and Nowotny,<sup>2</sup> who, on the grounds of powder data only, assigned the structure to the W<sub>5</sub>Si<sub>3</sub> type. A literature survey made by the author revealed that  $\alpha$ -V<sub>5</sub>As<sub>3</sub> is the only arsenide known to crystallize with this structure. The W<sub>5</sub>Si<sub>3</sub> type is otherwise represented by the Group V and Group VI silicides and germanides, by the Group IV and Group V gallides and also by a few rare-earth compounds.

One striking feature of this structure type is the occurrence of infinite linear chains running along the  $c$ -axis of the tetragonal cell for both kinds of atom. The interatomic distance in these chains is only 2.41 Å in the case of  $\alpha$ -V<sub>5</sub>As<sub>3</sub>, a remarkably short distance especially for arsenic. Short intermetallic distances are not uncommon in other metal-rich pnictides and chalcogenides. Close arsenic contacts are normally found only in arsenic-rich compounds, where, however, the As atoms never occur in a chain arrangement but form pairs or infinite networks.

Boller and Nowotny<sup>2,3</sup> observed a homogeneity range extending towards the metal-rich side, and syntheses made by the author confirmed this and indicated that the lattice

dimension variations affect the  $c$ -axis to the greatest extent.<sup>1</sup> This naturally leads to the assumption that a vacancy mechanism involving the occupancy of sites in the chains must play an important role.

This paper presents a single-crystal X-ray refinement, together with microprobe analyses, in an attempt to clarify the atomic distribution and to produce accurate values for the atomic coordinates as well as for the interatomic distances.

### EXPERIMENTAL

Vanadium (Materials Research Corp., 99.95 % pure) was arc-melted together with a specimen of the composition VAs<sub>0.88</sub> (prepared by a two-zone synthesis<sup>4</sup>), in an atmosphere of purified argon. The final product contained V<sub>2</sub>As,<sup>5</sup> V<sub>3</sub>As and only small amounts of  $\alpha$ -V<sub>5</sub>As<sub>3</sub>. The latter formed rod-like crystals in the matrix.

A well-shaped single crystal in the form of a parallelepiped was selected for collecting the X-ray intensity data. Its dimensions were 42 × 47 × 83 μm, its greatest extension being along the  $c$ -axis. The equipment and the intensity-collecting procedure were the same as in earlier studies.<sup>1,4</sup> Intensities were recorded up to  $2\theta=85^\circ$ , corresponding to  $0 \leq h \leq 18$ ,  $0 \leq k \leq 18$  and  $0 \leq l \leq 9$ . The instrumental stability, checked by three standard reflexions, was satisfactory.

Apart from Lp corrections, the single-crystal X-ray data were also corrected for absorption by a Gaussian grid method, the crystal being limited by faces of the forms {110} and {001}. The minimum and maximum transmission factors obtained were 0.272 and 0.326, using a calculated linear absorption coefficient of 345 cm<sup>-1</sup>.

Powder diffraction films recorded for the arc-melted alloy showed weak and diffuse  $\alpha$ -V<sub>5</sub>As<sub>3</sub> lines, particularly diffuse in the case of  $l=2$ . Evidently, the composition of the  $\alpha$ -V<sub>5</sub>As<sub>3</sub> phase varied appreciably within the

sample, making it necessary to determine both the composition and the lattice parameters for the particular crystal used for collecting the intensity data.

For the lattice parameter determination a General Electric "Single Crystal Orienter" equipped with  $\text{CuK}\alpha$  radiation was utilized. High-angle reflexions with a good  $\alpha_1$  to  $\alpha_2$  separation were measured for determining the Bragg angles. A least-squares refinement yielded the unit cell parameters (22 °C):  $a = 9.5031(4)$  Å and  $c = 4.8255(3)$  Å, assuming  $\lambda(\text{CuK}\alpha_1) = 1.540598$  Å and  $\lambda(\text{CuK}\alpha_2) = 1.544408$  Å. Corresponding four-circle data for  $\lambda(\text{MoK}\alpha) = 0.710688$  Å were:  $a = 9.500(2)$  Å and  $c = 4.830(2)$  Å.

Microprobe analyses were performed on single crystals only, including the one used for the intensity recordings as well as for the lattice dimension determination. The single crystals were embedded in a silver cement, precautions being taken to align a crystal surface perpendicular to the electron beam, since the instrument (Cambridge) was not equipped with any tilting or rotating facilities. The preparation technique introduces an angular error which is hard to avoid. Pure vanadium and arsenic, the latter being surface-treated with aluminium, were used as standards. As an extra check, measurements were also performed on VAs single crystals, prepared by chemical transport. Selte *et al.*<sup>4</sup> suggest a narrow range of composition of  $\text{VAs}_{1.00 \pm 0.02}$ , which is supported by the consistency of lattice parameter values given by various authors. A line sweep to investigate the homogeneity of the chosen area of a crystal face was followed by five spot measurements for each element. The microprobe intensity data were corrected for the effects of atomic number, fluorescence and absorption by the MK 13 program obtained from the Geological Survey of Sweden.<sup>7</sup> The estimated relative accuracy was 5 %.

The numerical calculations were performed using IBM 370/155 and IBM 1800 computers. The crystallographic programs for the structure analysis are described in Ref. 8.

## STRUCTURE REFINEMENT

The coordinates given by Boller and Nowotny<sup>2</sup> were used as the starting parameters for a series of full-matrix least-squares refinements, together with one scale factor and isotropic temperature factors. The space group  $I4/mcm$  was assumed, and the scattering factors, including dispersion corrections, were taken from Ref. 9.

The agreement obtained after convergence was rather poor, with a conventional  $R(F)$  of 0.12. A data survey revealed that the  $F_o/F_c$

ratio was near unity for reflexions with odd  $l$ , while those with even  $l$  showed severe disagreement between  $F_o$  and  $F_c$ . Indeed, another refinement, restricted to reflexions with  $l$  odd, converged to  $R(F) = 0.05$ . These reflexions are insensitive to the occupation in the  $z = 1/4$  plane. A difference Fourier map was calculated for this plane to find out whether there were other peaks than those corresponding to the special positions  $4a$  and  $4b$ , but it only revealed that anisotropic thermal parameters were required. The introduction of these made  $R(F)$  drop drastically.

The occupancies of the  $4a$  and  $4b$  positions were allowed to vary. Only the  $4a$  position assigned to the arsenic atoms was affected significantly. Extinction effects were taken care of by a method devised by Coppens and Hamilton.<sup>10</sup> The final refinements were made on  $F^2$  rather than  $F$  so as to include reflexions with "negative intensities".<sup>11</sup> The equivalent ( $hkl$ ) and ( $khl$ ) reflexions were all included (845 refl.) and not averaged as in the early stages of refinement so as to take care of the extinction effects properly. The final agreement factors were  $R(F^2) = 0.027$  and  $R_w(F^2) = 0.044$ , with the corresponding  $R(F) = 0.028$ , where

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

The weights were assigned according to  $w^{-1} = \sigma_c^2(F_o^n) + (p_n|F_o^n|)^2$ , with  $p_2 = 0.02$ .  $\sigma_c(F_o^n)$  is

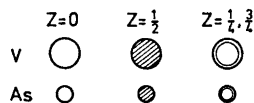
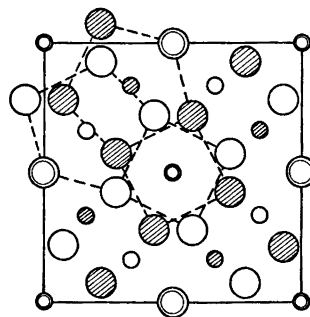


Fig. 1. The structure of  $\alpha\text{-V}_5\text{As}_3$  projected on (001).

Table 1. Structure data for  $\alpha$ -V<sub>5</sub>As<sub>2.74</sub>, including anisotropic thermal parameters  $U_{ij}$  ( $\times 10^6$ ) Å<sup>2</sup>. The form of the temperature factor is  $\exp[-2\pi^2 a^{*2} (U_{11}h^2 + U_{22}k^2 + 2U_{12}hk) - 2\pi^2 U_{33}l^2 c^{*2}]$ ;  $U_{13} = U_{23} = 0$ . Standard deviations within brackets. Space group:  $I4/mcm$  (No. 140).

Atom	Position	Occupancy (%)	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$
V(1)	16k	100	0.07601(3)	0.22405(3)	0	520(10)	677(11)	1005(12)	77(7)
V(2)	4b	100	0	$\frac{1}{2}$	$\frac{1}{2}$	498(11)	$U_{11}$	467(19)	0
As(1)	8h	100	0.16458(2)	$x + \frac{1}{2}$	0	425(6)	$U_{11}$	880(11)	-33(6)
As(2)	4a	74.3(2)	0	0	$\frac{1}{2}$	503(15)	$U_{11}$	9580(84)	0

the standard deviation of  $F_o^n$  based on counting statistics, and  $p_n$  is an empirical factor accounting for instrumental errors. A  $\Delta R$  normal probability plot<sup>12</sup> gave the slope 0.95 and an intercept of -0.10, which shows that the intensity material was not too heavily affected by systematic errors.

The structural parameters from the last  $F^2$  refinement are given in Table 1. The structure factors can be obtained on request from the author.

## DISCUSSION

In the least-squares refinement, three parameters are sensitive to the intensities of strong reflexions with even  $l$ : the anisotropic temperature factors, the extinction factor and the occupancy of the 4a and 4b positions. It is comforting to note that the refinement showed rather weak correlations between these parameters; the greatest correlation was 0.59 between the occupancy of 4a and the corresponding  $U_{11}$ . The refinement clearly showed that only the occupancy of the 4a position (arsenic) and not the 4b position (vanadium) is affected, entirely in line with expectations. The large apparent thermal motion of As(2) in the  $c$ -direction is probably an indication as to small random deviations from the value of  $z = 1/4$

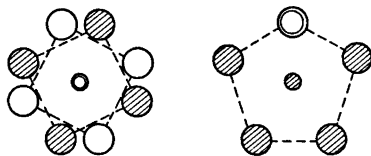


Fig. 2. Coordination polyhedra around arsenic, corresponding to the coordination numbers 8 (left) and 6 (right). Notation similar to Fig. 1.

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caused by the vacancies. Unfortunately, there is an additional problem. It cannot be concluded with certainty from this study whether 4a is occupied to 74 % by arsenic as indicated by the refinement, or whether it has a mixed occupation of both kinds of atom so as to give the corresponding scattering power as suggested by Boller and Nowotny.<sup>8</sup> A neutron diffraction study is planned in order to resolve this ambiguity. At the present stage, the composition is assumed to be V<sub>5</sub>As<sub>2.74</sub>, i.e. 55.4 % V and 44.6 % As. The microprobe analyses on the same crystal yielded 57.2 % V and 42.8 % As. In view of the experimental difficulties, these values agree very well - within 4 % - with the crystallographic data as interpreted in terms of arsenic vacancies only.

A projection of the  $\alpha$ -V<sub>5</sub>As<sub>3</sub> structure is shown in Fig. 1. The interatomic distances in  $\alpha$ -V<sub>5</sub>As<sub>2.74</sub> are given in Table 2. As(2) coordinates eight vanadium atoms in a slightly irregular square antiprismatic arrangement (Fig. 2). In fact, no W<sub>5</sub>Si<sub>3</sub>-type compound

Table 2. Interatomic distances (Å) and coordination in  $\alpha$ -V<sub>5</sub>As<sub>2.74</sub>. The maximum standard deviation obtained was 0.0006 Å. Distances shorter than 3.5 Å are listed.

V(1)-As(1)	2.520	As(1)-2V(2)	2.519
As(1)	2.529	2V(1)	2.520
2As(2)	2.551	2V(1)	2.529
V(1)	2.687	4V(1)	2.766
2As(1)	2.766	2As(1)	3.331
2V(1)	2.812		
2V(2)	2.976	As(2)-2As(2)	2.413
2V(1)	3.127	8V(1)	2.551
2V(1)	3.179		
V(2)-2V(2)	2.413		
4As(1)	2.519		
8V(1)	2.976		

presents a regular antiprism. As(1) has six vanadium neighbours at fairly even distances in an arrangement (Fig. 2) similar to what is found in the  $Nb_4As_3$  type,<sup>13</sup> but in  $\alpha-V_5As_3$  there are four additional atoms only slightly further away. The V(2) atoms form a straight chain, extending infinitely in the *c*-direction. Such metal chains with short intermetallic distances are also found in the  $Cr_3Si$  structure type  $-V_3As$  being an example – a class of compounds often showing superconductivity explained by a Barisic-Labbé-Friedel linear-chain model, which exhibits strong transition metal *d*-electron overlap.<sup>14</sup> It seems that very few investigations have been performed on the possibility of superconductivity among the  $W_6Si_3$ -type compounds.  $Nb_6Ga_3$  has a  $T_c$  of 1.35 K,<sup>15</sup> while  $V_6Si_3$  shows no superconducting behaviour down to 0.3 K.<sup>16</sup> The  $V_6Si_3$  structure type<sup>17</sup> is another example of a crystal structure characterized by infinite linear metal chains with short intermetallic distances. Attempts to detect superconductivity above 1.5 K for the isostructural  $V_6Si_3$  and  $Ti_6Ge_3$  failed.<sup>18</sup>

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