Crystal Structure Refinement of $\alpha$-V$_4$As$_3$

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The crystal structure of $\alpha$-V$_4$As$_3$ 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$_5$Si$_3$. 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$_4$As$_3$. Two of these, $\beta$-V$_4$As$_3$ and $\gamma$-V$_4$As$_3$, are stable only at elevated temperatures, while $\alpha$-V$_4$As$_3$ also forms in silica-tube syntheses. The latter phase was first reported by Boller and Nowotny, who, on the grounds of powder data only, assigned the structure to the W$_5$Si$_3$ type. A literature survey made by the author revealed that $\alpha$-V$_4$As$_3$ is the only arsenide known to crystallize with this structure. The W$_5$Si$_3$ 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$_4$As$_3$, 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 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. 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$_{50}$ (prepared by a two-zone synthesis), in an atmosphere of purified argon. The final product contained V$_4$As$_5$, V$_4$As and only small amounts of $\alpha$-V$_4$As$_3$. 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 $42 \times 47 \times 83$ μm, its greatest extension being along the $c$-axis. The equipment and the intensity-collecting procedure were the same as in earlier studies. 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 reflections, 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$^{-1}$.

Powder diffraction films recorded for the arc-melted alloy showed weak and diffuse $\alpha$-V$_4$As$_3$ lines, particularly diffuse in the case of $l=2$. Evidently, the composition of the $\alpha$-V$_4$As$_3$ 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"
was utilized. High-angle reflexions with a good z, to z, separation
were measured for determining the Bragg
angles. A least-squares refinement yielded the
unit cell parameters (22°C): a = 9.5003(4) Å
and c = 4.8255(3) Å, assuming λ(CuKα) =
1.540598 Å and λ(CuKα) = 1.544408 Å. Cor-
responding four-circle data for λ(MoKα) =
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 angu-
lar error which is hard to avoid. Pure vanadium
and arsenic, the latter being surface-treated
with aluminium, were used as standards. As
a double check, measurements were also per-
formed on VAs single crystals, prepared by
chemical transport. Selte et al.4 suggest a narrow
range of composition of VAs₁₋ₓAsₓ, which is
supported by the consistency of lattice param-
eter 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.5
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 No-
nowtyny* were used as the starting param-
eters for a series of full-matrix least-squares refine-
ments, 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 F₀/F₉
ratio was near unity for reflexions with odd l,
while those with even l showed severe dis-
agreement between F₀ and F₉. 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.16 The final refinements were made
on Fₙ rather than F₀ so as to include reflexions
with "negative intensities".17 The equivalent
(hkl) and (hkln) 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(Fₙ) = 0.027 and Rₐ(Fₙ) = 0.044,
with the corresponding R(F) = 0.028, where

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

and

\[ R_\alpha(F^n) = \frac{\sum w|F_o^n| - |F_c^n|^\alpha}{\sum w|F_o^n|^\alpha} \]

n = 1, 2

The weights were assigned according to w⁻¹ =
\( \sigma_c^2(F_o^n) + (p_σ|F_o^n|^4) \), with \( p_σ = 0.02 \). \( \sigma_c(F_o^n) \) is

\[ \sigma_c = \frac{1}{\sqrt{N}} \]

Fig. 1. The structure of \( \alpha-V_4As_4 \) projected on
(001).

Table 1. Structure data for \( \alpha-V_4As_3S_4 \), including anisotropic thermal parameters \( U_{ij} \times 10^4 \) \( \text{Å}^2 \). The form of the temperature factor is \( \exp[-2\pi^2u_{ij}(U_{11}h^2 + U_{22}k^2 + 2U_{12}hk) - 2\pi^2u_{22}P_c^2 \cdot \text{Å}^2] \); \( U_{13} = U_{23} = 0 \). Standard deviations within brackets. Space group: \( I4/mcm \) (No. 140).

<table>
<thead>
<tr>
<th>Atom</th>
<th>Position</th>
<th>Occupancy (%)</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>( U_{11} )</th>
<th>( U_{22} )</th>
<th>( U_{33} )</th>
<th>( U_{12} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>V(1)</td>
<td>16( k )</td>
<td>100</td>
<td>0.07600(3)</td>
<td>0.22405(3)</td>
<td>0</td>
<td>520(10)</td>
<td>677(11)</td>
<td>1005(12)</td>
<td>77(7)</td>
</tr>
<tr>
<td>V(2)</td>
<td>4( b )</td>
<td>100</td>
<td>0</td>
<td>0.5</td>
<td>0.5</td>
<td>488(11)</td>
<td></td>
<td>467(19)</td>
<td></td>
</tr>
<tr>
<td>As(1)</td>
<td>5( h )</td>
<td>100</td>
<td>0.16458(2)</td>
<td></td>
<td>0.5</td>
<td>425(6)</td>
<td></td>
<td>880(11)</td>
<td>-33(6)</td>
</tr>
<tr>
<td>As(2)</td>
<td>4( a )</td>
<td>74.3(2)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>503(15)</td>
<td></td>
<td>9350(84)</td>
<td></td>
</tr>
</tbody>
</table>

The standard deviation of \( F_o \) based on counting statistics, and \( p_o \) is an empirical factor accounting for instrumental errors. A \( \Delta R \) normal probability plot 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 4\( a \) and 4\( b \) 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 4\( a \) and the corresponding \( U_{11} \). The refinement clearly showed that only the occupancy of the 4\( a \) position (arsenic) and not the 4\( b \) 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 \( z=1/4 \) caused by the vacancies. Unfortunately, there is an additional problem. It cannot be concluded with certainty from this study whether 4\( a \) 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. A neutron diffraction study is planned in order to resolve this ambiguity. At the present stage, the composition is assumed to be \( V_5As_3S_4 \), 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 \( \alpha-V_4As_3S_4 \) structure is shown in Fig. 1. The interatomic distances in \( \alpha-V_4As_3S_4 \) are given in Table 2. As(2) coordinates eight vanadium atoms in a slightly irregular square antiprismonic arrangement (Fig. 2). In fact, no \( W_6Si_4 \)-type compound

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

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 Nb₄As₄ type, but in α-V₄As₄ 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 Cr₃Si structure type ‒ V₄As 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. It seems that very few investigations have been performed on the possibility of superconductivity among the W₄Si₄-type compounds. Nb₃Ga₄ has a Tₐ of 1.35 K, while V₄Si₄ shows no superconducting behaviour down to 0.3 K. The V₄Si₄ structure type 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 V₄Si₄ and Ti₄Ge₄ failed.

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REFERENCES


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