

Preparation of Single Phases and Single Crystals in the Vanadium-Gallium-Antimony System. Crystal Structure of V_6GaSb

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

Vanadium-antimony and vanadium-gallium-antimony compounds were prepared by floating zone melting. Single phases of A15 structure were produced for both the V–Sb and the V–Ga–Sb systems. Samples were examined by X-ray diffraction and X-ray fluorescence analysis. A single crystal of nominal composition V_6GaSb was mounted on a four-circle diffractometer for a detailed investigation of order parameters. The A15 structure, space group $Pm\bar{3}n$, was confirmed. Ga and Sb are distributed at random at the positions 0,0,0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. The vanadium atoms are in an ordered arrangement in the $0, \frac{1}{2}, \frac{1}{4}$ positions. A conventional R -value of 0.8% was obtained. Deviations from stoichiometry are discussed. Attempts to introduce In atoms in the A15 structure by reacting V with InSb were unsuccessful.

Vanadium forms a number of intermetallic compounds of general formula $V_{3+y}X$. Several are of A15 structure. The stoichiometry range, defined by the possible values of y , is in general difficult to assess, partly because equilibria are established very slowly at low temperature. The best investigated compound of this class is probably V_3Ga , an important superconductor. Little is known about V_3Sb and we therefore chose to investigate this compound and part of the V_3Ga-V_3Sb system. V_3Ga is stable at both sides of the stoichiometric composition. We found that the stoichiometric range for $V_{3+y}Sb$ also extends to both positive and negative values of y , and we examined the possibility of producing a pure phase of stoichiometry V_6GaSb . General phase diagram considerations indicate that it should be possible to establish a

V_3X phase of 25 atomic percentage X in the V_3Ga-V_3Sb pseudo binary system and also one in which $X = \frac{1}{2}Ga + \frac{1}{2}Sb$.

EXPERIMENTAL

The compounds were in general synthesized from pure elements by induction heating in a helium atmosphere. We made GaSb using a graphite crucible and the other compounds using crucible-free methods. Powder mixtures of nominally 99.5% V and 99.9% Sb were pressed into nearly cylindrical rods by isostatic pressing. A rod of composition $3V + 1Sb$ was sintered in a helium atmosphere of 0.35 MPa at about 800 °C. Afterwards a molten zone of width 10–15 mm and of temperature 1425 °C was passed through the sample at a speed of about 10 mm/h. The helium pressure was 1.5 MPa in this run. The sample lost 3.7% of weight as some Sb evaporated. Another specimen, of composition $3V + 1.5Sb$ was treated in a similar way. Also here some Sb evaporated. Powder mixtures of V and GaSb were pressed, sintered and zone melted as already described and attempts were made to react V and InSb, both in the induction oven and in a high temperature powder diffractometer.

The zone melted rods were cut perpendicular to the cylinder axis into sections using a spark cutting machine. We took samples from the sections by filing with a diamond file and examined the powders by X-ray diffraction using a Guinier camera and in some cases also a powder diffractometer. The cylindrical sections were next ground and polished and examined by metallographic techniques and finally analyzed by X-ray fluorescence analysis.

Measurements and computations were performed essentially in the same way as described by Vicente and Rasmussen.¹ Pure Sb was used as reference sample for antimony for the V_3Sb case and GaSb was used as reference for the V_6GaSb samples. Excitation voltages were chosen near the K -absorption edge for each element to avoid secondary enhancement effects. The α -coefficients (Ref. 1) were calculated assuming that the absorption edge was the effective wavelength for each element determined. As a control of the relevance of the absorption coefficients employed the composition of GaSb was determined using pure Ga and pure Sb, respectively, as reference samples. (Found: Ga 36.34; Sb 63.48. Calc.: Ga 36.41; Sb 63.59). Vanadium was not analyzed by fluorescence analysis. One sample was analyzed for vanadium by redox titration of V^{4+} with Fe^{2+} .

Semiconductor grade germanium was used for calibrating Guinier films, assuming a lattice constant $a=5.6576$ Å. The wavelength of the $CuK\alpha_1$ radia-

tion used with the camera was taken to be 1.54051 Å.

We selected single crystals of V_6GaSb from crushed fragments and investigated them by X-ray diffraction. Graphite monochromatized radiation was employed with Weissenberg and precession cameras to establish space group and crystal quality. The apparently best suited crystal of those examined was mounted on a Picker fourcircle diffractometer. We collected 598 reflections using $MoK\alpha$ radiation selected by a graphite monochromator. A scintillation detector was employed in conjunction with a pulse height analyzer.

The crystal was a rod of $0.017 \times 0.017 \times 0.197$ mm, $\mu(MoK\alpha)$ is 227.5 cm^{-1} . An absorption correction was applied and gave transmission factors in the range 0.65–0.71. The data were averaged according to the symmetry $m3m$ with an internal agreement of 0.04 giving 48 independent reflections of which only 30 were significant ($I > 3\sigma I$). The X-ray photographs and the diffractometric measurements confirmed the cubic symmetry and the systematic extinctions were

Table 1. Analytical and other results for V–Sb preparations. Samples labelled 271076 were prepared from mixtures of stoichiometry 3 V + 1 Sb before melting. Samples labelled 170976 were prepared from mixtures of stoichiometry 3 V + 1.5 Sb. Estimated standard deviations of a : 0.002 Å. Estimated standard deviation of chemical analysis: 0.1 %.

Sample No.	w % V	w % Sb	Density g cm^{-3}	Lattice const. Å	Formula	Ref.
271076–						
2		39.73		4.938	$V_{3.63}Sb$	This paper
3			6.889	4.941	$V_{3.75}Sb$	– –
a	57.4	39.66		4.937	$V_{3.64}Sb$	– –
b	57.4	37.09		4.937	V_4Sb	– –
170976–						
2				4.945		– –
3				4.940		– –
4		46.08	7.35	4.942	$V_{2.8}Sb$	– –
				4.932		2
				4.9335		3
				4.941		4

Table 2. Analytical and other results for V–Ga–Sb phases. Original stoichiometry before melting was 6V + Ga + Sb. Estimated standard deviation of a : 0.002 Å. Estimated standard deviation of chemical analysis: 0.1 %.

Sample No.	w % Ga	w % Sb	Density g cm^{-3}	Lattice const. Å	Formula
291076–					
2	15.54	22.12		4.893	
3	16.31	22.43		4.892	$V_6Ga_{1.12}Sb_{.88}$
4	17.47	23.8	6.904	4.892	$V_6Ga_{1.22}Sb_{.95}$

Table 3. Lattice constants for V_3Ga , V_3Sb and V_6GaSb .

Compound	<i>a</i>	σa	Ref.
V_3Ga	4.818	.001	5
V_6GaSb	4.892	.002	This paper
V_3Sb	4.940	.002	– –

consistent with the space group $Pm\bar{3}n$ (No. 223) to which the A15 structure is assigned.

The majority of the V–Sb samples were badly suited for X-ray fluorescence analysis as most of the slices cut from the zone melted rods were porous but a few were completely homogenous. Table 1 shows analytical results and observed lattice constants for V–Sb compounds. It is evident that the diffraction technique applied is not sensitive enough to indicate analytical composition. The table also shows that the existence range for the A15 structure is at least in the range of 21.6 to 26.3 atomic percent Sb. Table 2 shows similar results for the V–GaSb products. It is again obvious that chemical composition cannot be established from observed lattice constants but that a chemical analysis is necessary.

Our attempts to react vanadium with In by sintering or by melting vanadium with InSb were unsuccessful. Sintered products yielded at room temperature powder diagrams which showed the presence of metallic In and a phase of A15 structure with a lattice constant equal to that of V_3Sb . Samples which had been subjected to zone melting were nearly depleted of their In content as shown by X-ray fluorescence analysis. According to their powder diagrams they were pure phases of V_3Sb structure. For comparison lattice constants of V_3Ga , V_3Sb and V_6GaSb are shown in Table 3.

RESULTS AND DISCUSSION

As a check we calculated a three dimensional Patterson function which was in full agreement with the proposed A15 structure. Thus, the main problem was to determine the degree of order of the atomic arrangement. For this discussion the following considerations are helpful:

In a compound of formula A_3B and space group $Pm\bar{3}n$ the atoms occupy the positions:

A: 0,1/2,1/4; etc. (6-fold)

B: 0,0,0; 1/2,1/2,1/2 (2-fold)

The structure factors may for convenience be arranged in the following categories:

I: $h+k+l=2n+1$, with contributions from A-atoms only, and

II: $h+k+l=2n$, with contributions from A- and B-atoms.

In category I the following types of reflections are extinguished:

$$h=2n+1, k=2n+1, l=2n+1$$

$$h=4n, k=4n, l=2n+1$$

$$h=4n+2, k=4n+2, l=2n+1.$$

The reflections with $h=4n+2, k=4n, l=2n+1$ are generally strong with $F(hkl)=4f_A$.

Category II reflections yield the following structure factors:

$$F=2(f_B-f_A) \text{ for } h=k=2n+1, l=4n$$

$$F=2(f_B+f_A) \text{ for } h=k=2n+1, l=4n+2$$

$$F=2f_B \pm 6f_A \text{ for the rest of category II.}$$

Reflections which should be systematically absent were especially carefully examined, both by photographic methods and by counter measurements; none were observable. A model assuming an ordered arrangement of Ga and Sb atoms on the B-sites could therefore be excluded. Since we could observe and measure reflections with $h=k=2n+1, l=4n$ we could also exclude a model assuming a completely disordered arrangement of all V, Ga and Sb atoms. Intermediate degrees of order were examined by least-squares refinement of various models. The scattering factors used were those published in Volume IV of International Tables for X-Ray Crystallography. Although we could discard the assumption of an ordered arrangement of Ga and Sb atoms, we did try a refinement of such a model allowing a site occupation parameter to vary. The refinement yielded a parameter value corresponding to equal occupancy of the 0,0,0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ positions.

The possibility of Ga and Sb atoms occupying part of the A-sites instead of vanadium was tested refining the site occupation parameter of the vanadium position. The highest value of this parameter was 1.01 for a model assuming equal amounts of Ga and Sb on the B-sites with full occupancy. Models assuming deficit of Sb gave occupation parameters slightly less than 1. We are not certain about the composition of the particular crystal fragment employed in this analysis but it is most likely to be of a composition near $V_6Ga_{1.12}Sb_{0.88}$; cf. Table 2. Thus we consider the A-sites to be fully ordered and

Table 4. Results of two refinements: (a) where the occupation factor for V was kept at 1.0 and (b) where the ratio Ga:Sb was kept at the value 0.56:0.44 found by fluorescence analysis, both with full occupation of the B-sites.

	a	b
<i>Occ</i> (V)	1.0	0.978(5)
U_{11} (V)	0.0086(4)	0.0086(4)
U_{33} (V)	0.0067(4)	0.0067(4)
<i>Occ</i> (Ga)	0.510(10)	0.56
<i>Occ</i> (Sb)	0.490	0.44
U (Ga,Sb)	0.0066(3)	0.0065(3)
Scale factor	0.1802(16)	0.1843(13)
Extinction param.	0.00127(16)	0.00131(16)
Minimum transmiss.	0.82	0.82
$R(F)$	0.0084	0.0084
$R(F^2)$	0.0162	0.0162

occupied by V-atoms within experimental uncertainty. According to site symmetry the vanadium atom may have two different thermal parameters, U_{11} and U_{33} . The GaSb atoms must vibrate isotropically. The introduction of the parameter allowing for anisotropic motion of the vanadium atom lowered the R -value from 1.0% to 0.8% for two models which differ slightly in stoichiometry but otherwise are similar. Table 4 shows the results from the refinements which yielded the lowest R -values. Although the R -value is fairly satisfactory the data do not allow an accurate determination of stoichiometry. It appears, however, that it is likely that Sb is present in less than the stoichiometric amount. The uncertainty about stoichiometry is of little consequence for the thermal parameters. The two models a and b of Table 4 yield practically the same u -values. The lighter V atom has the larger movement, but not as much as could be expected from the difference in mass. This is due to the close contacts in the V chain, which also lead to the movement along the chain being less than perpendicular to it, as was also found in V_3Si .⁶

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