

Variation of Lattice Parameters in TiS-VS Solid Solutions

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Received May 13, 1974

Results of measurements of lattice parameters and densities in nonstoichiometric solid solutions of titanium and vanadium monosulfide are reported and discussed. The results indicate that a second-order phase transition from the NiAs-type of MnP-type structure occurs at an intermediate composition, and that the phase transition is accompanied by a marked change in the rate of change of the metal-metal distances in the *c*-axis direction.

Introduction

The importance of relatively short metal-metal distances in the NiAs-type structure has been discussed previously by a number of authors (1-3), but few if any experiments have been performed with the purpose of examining the effect of changing composition upon these distances. It has been previously noted by one of the present authors (4) that the Ti-Ti distance along the *c*-axis in TiS with the NiAs-type structure is relatively large (3.19 Å) (5) and this large distance was used as a basis for questioning the importance of metal-metal interactions to the stability of this compound. The V-V distance in the *c*-axis direction in stoichiometric VS, on the other hand, is about 0.25 Å (6) shorter than the Ti-Ti distance in TiS. These observations provided the motivation for the examination of the lattice parameters and phase behavior in TiS-VS solid solutions to obtain information about the course of changes in the metal-metal distances along the *c*-axis direction with changing V/Ti.

Furthermore, stoichiometric VS crystallizes with the MnP-type structure (7), whereas TiS crystallizes with the NiAs-type structure. The phase transition in VS from NiAs-type to MnP-type is accompanied by a distinct decrease in the metal-metal distances in the

x-y plane (8) and has been observed to occur as a second-order phase transition (9). It is therefore of interest to observe the behavior of the phases in the VS-TiS solid solution region in order to observe the effect of the phase transition upon the changes in the lattice parameters.

Experimental

Samples of $Ti_xV_{1-x}S$, were prepared from high-purity vanadium (>99.99%) and titanium (>99.95%) metals. The metals were filed in an argon filled dry box and the particles were cleansed of macroscopic magnetic impurities by exposure to a strong magnetic field. The metal particles were mixed in weighed amounts with high purity sulfur (>99.99%) and the stoichiometric mixtures were sealed in evacuated Vycor tubes. After three days in a resistance furnace at 750°C the tubes were quenched and opened. The contents were pelleted and heated in an inductively heated tungsten crucible in high vacuum ($>10^{-5}$ Torr) at 1250°C for several hours. The resulting partially annealed pellets were arc-melted in an inert atmosphere and annealed again at temperatures between 1400 and 1600°C. Samples thus prepared were investigated in three ways. Guinier powder diffraction patterns were obtained from the quenched samples using $CuK\alpha$ radiation, sample

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densities were determined using a 10 cm³ pycnometer with distilled water as the displaced fluid and sample weights of the order of 0.5 g, and chemical compositions were determined by X-ray emission electron microprobe analysis using VS_{1.04} and Ti metal as standards. Analyses were performed only on those sections of samples which were able to accept mechanical polishing. Areas showing voids or roughness were avoided. The analyses were run using the following X-ray lines for analysis: S, $K\alpha_{1,2}$; Ti, $K\alpha_{1,2}$; V, $K\beta_1$. The primary beam voltage was maintained at 10 kV using a static beam and the beam power was monitored with a 417 Keithley picoammeter under suppression. Three separate points were analyzed on one portion of each sample. Four integrated measurements were made at each point. Detailed microprobe scans of several individual samples were performed to assure that the bulk samples were homogeneous to within the limits of uncertainty of the method.

The uncertainty in composition at the 95% confidence level was 0.15 at %.

The lattice parameters were determined by least-squares calculation using the powder diffraction data. The uncertainties in the parameters, estimated by the method of propagation of errors, are ± 0.003 Å for a , ± 0.002 Å for b , and ± 0.005 Å for c . The uncertainties in the pycnometrically measured densities are estimated to be ± 0.05 g cm⁻³.

Results

The results obtained are presented in the Table I. Although each sample was prepared with the goal of obtaining $y = 1.00$, this goal was not reached. The preparation procedure, which required the various high-temperature treatments described above in order that homogeneous samples be produced, resulted in samples for which the sulfur-to-metal ratio varied between 0.91 and 1.20. The deviations

TABLE I
SUMMARY OF DERIVED AND EXPERIMENTAL RESULTS

Sample No.	X	Structure	S/M	Lattice parameters			Density
				A	B	C	
3	0.880	NiAs	0.990	3.314	—	6.274	4.50
5	0.787	NiAs	1.010	3.328	—	6.196	—
21	0.737	NiAs	1.064	3.347	—	6.094	4.40
6	0.687	NiAs	0.948	3.355	—	6.077	—
29	0.685	NiAs	1.075	3.354	—	6.063	4.46
28	0.681	NiAs	1.114	3.357	—	6.049	4.59
27	0.674	NiAs	1.126	3.358	—	6.043	4.54
31	0.634	MnP	1.103	3.353	5.852	6.031	4.38
20	0.620	MnP	1.092	3.366	5.803	6.016	4.47
30	0.612	MnP	1.092	3.353	5.819	6.030	—
5	0.584	MnP	1.069	3.343	5.837	6.025	4.54
19	0.545	MnP	1.018	3.337	5.886	5.990	4.71
8	0.502	MnP	1.079	3.347	5.847	6.000	—
9	0.400	MnP	0.969	3.342	5.853	5.966	4.65
17	0.357	MnP	1.149	3.342	5.848	5.939	—
11	0.287	MnP	0.918	3.334	5.839	5.921	4.81
16	0.262	MnP	1.200	3.334	5.844	5.915	4.77
12	0.192	MnP	0.909	3.333	5.837	5.909	4.85
15	0.165	MnP	1.170	3.323	5.837	5.880	4.70
13	0.118	MnP	0.963	3.331	5.823	5.891	4.83
14	0.040	MnP	0.929	3.313	5.831	5.875	4.92

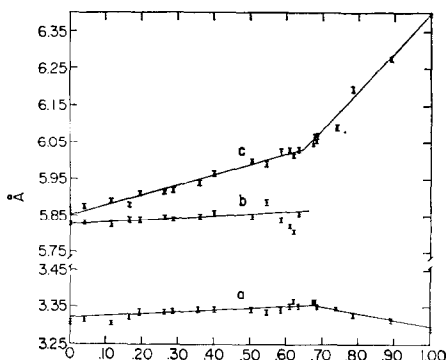


FIG. 1. Lattice parameters vs composition. Composition is expressed as x in $Ti_xV_{1-x}S$ and the axes are labeled so that the a and c axes are those continuous with the NiAs a and c axes, respectively, while the b axis refers to the third orthorhombic axis.

of the sulfur-to-metal ratios from the desired value were presumably primarily due to the vaporization of the components at the very high temperatures of molten material in the arc melter. All samples more titanium-rich than $x = 0.66$ exhibited the NiAs-type structure or were two-phase mixtures of the NiAs-type phase and a Ti_8S_9 -type phase (10). Samples containing the Ti_8S_9 -type phase were eliminated from further consideration.

The lattice parameters exhibited a regular variation with x , as can be seen in Fig. 1, in

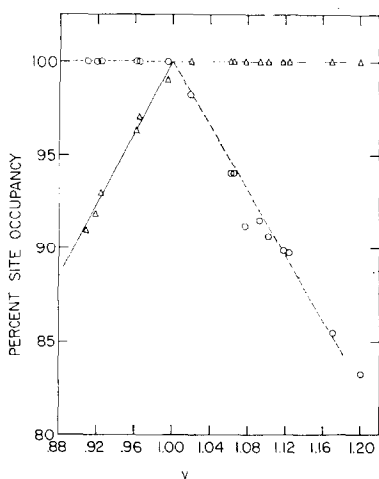


FIG. 2. Percent site occupancy vs y . The figure indicates the correlation of site occupancy with sulfur content. \circ Metal; Δ non-metal.

spite of irregular variations in y (column 4 of Table I). The densities, compositions, and lattice parameters were used to calculate the fractional occupancies of the metal and non-metal positions, assuming that vacancies were the only defects. The percent occupancies are shown plotted vs y in Fig. 2.

Discussion

The lattice parameter variations in Fig. 1 are consistent with a second-order symmetry change between the hexagonal, NiAs-type, structure and the orthorhombic, MnP-type, structure at $x = 0.66$. The decrease in the c -axis with substitution of V for Ti is rather large (1 Å per mole substituted) and is significantly greater in the NiAs-type structure than in the MnP-type structure, as can be seen in Fig. 1. Also, it can be seen that the a -axis increases with substitution of V for Ti in this region.

In the MnP-type structure the metal atoms do not lie along the c -axis and thus the increase in the metal-metal distance along the c -axis direction in phases with this structure is less than the increase in the length of the c -axis. Thus, the increase in the slope of the c -axis vs x at the phase transition from the MnP-type to NiAs-type structure demonstrates that the increase in the metal-metal distance along the c -axis with substitution of V by Ti is significantly greater in phases with the NiAs-type structure than in phases with the MnP-type structure. It is therefore interesting to note that the metal-metal distances within the a - b plane increase significantly in the second-order transition to the MnP-type phase (8), indicating that increasing metal-metal distances accompany the substitution of V by Ti in the monosulfide, along the c -axis in the NiAs-type phase and principally within the a - b plane in the MnP-type phase.

Conclusions

The lattice parameters in the nonstoichiometric compounds $Ti_xV_{1-x}S_y$, with the NiAs-type structure vary with x , and essentially not with y , such as to demonstrate that a principal effect of substitution of Ti for V is to signifi-

cantly increase the metal-metal distances along the *c*-axis. The changes in the slopes of the parameters at the NiAs → MnP transition indicate that a second-order phase transition occurs, and that the marked decrease in the metal-metal distances along the *c*-axis for the NiAs-type solids is not important in the MnP-type solids.

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