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The NiAs–MnP Phase Transition in VS

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Results of measurements of the lattice parameters, magnetic susceptibility, and electrical resistivity of stoichiometric VS as functions of temperature through the MnP–NiAs transition region are reported and discussed. The properties are found to be consistent with a metallic solid in which the Fermi energy passes through a marked change in the density of states with the concurrent formation of zigzag metal chain in the *a–b* plane.

Introduction

Vanadium monosulfide has been studied by crystallographic techniques (*1*, *2*) and by NMR (*3*) and the observed crystal-structure change from NiAs-type to MnP-type was shown to occur continuously with changing vanadium to sulfur ratio (V/S), within the limits of resolution of the techniques. A recent analysis (*4*) of the symmetry change has shown that a second-order phase transition is consistent with Landau's theory (*5*) in this case.

It is of interest to examine the properties of a solid undergoing a continuous distortion because such a change provides a simplification in the consideration of the relationship between structure and properties. The continuity of the distortion makes it possible to follow properties such as electrical conductivity and magnetic susceptibility through the symmetry change, and to observe the simultaneous change in structure and properties without the obscuring consequences of a discontinuous change in the relative positions of the atoms in the solid and the consequent phase separation.

The work reported here was done to determine the variation of lattice parameters, electrical conductivity, and magnetic susceptibility of solid stoichiometric vanadium monosulfide with temperature, particularly through the MnP-type to NiAs-type phase transition.

Experimental

The VS used for property measurements was prepared from high purity (99.99%) sulfur and vanadium metal prepared and analyzed by groups at the Ames Laboratory of the U.S.A.E.C., Ames, Iowa. The impurity levels in a vanadium bulk sample were found to be: Si, 300 ppm; O, 280 ppm; Al, 100 ppm; C, N, Ni, Fe, and Mg, all less than 60 ppm. Metal particles obtained from the bulk sample by filing were analyzed by Mr. A. Meetsma, and the result was 100.08% V, indicating that negligible contamination resulted from the filing. The metal particles were placed in a sealed quartz tube together with a stoichiometric amount of sulfur, and the tube was heated at temperatures up to 700°C for about one week. The sulfur to vanadium ratios in the resultant samples were determined by Mr. A. Meetsma to be within 1% of unity.

X-ray diagrams were taken of a sample at room temperature with a powder diffractometer (Philips) and at high temperature with a

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Guinier–Lenné camera (Nonius). The temperature of the sample was varied continuously between room temperature to above the transition temperature. The sample was sealed in very thin walled, evacuated quartz capillaries to prevent oxidation of the sample, and the sample chamber was at a residual pressure of about 10^{-2} Torr. The sample was heated at a rate of about 10°/hr.

Differential thermal analysis was performed with an apparatus constructed by Dr. J. C. Wildervanck and Mr. J. Koopstra. The heating rate was about 10°/min. Magnetic measurements were carried out using a Faraday balance constructed by Dr. C. F. van Bruggen. The balance has been briefly described previously (*6*). Susceptibilities were measured at 52 different temperatures in the interval between room temperature and about 850°C. Data were collected with both increasing and decreasing temperatures in approximately equal numbers. The electrical resistivity was measured by the four-probe method using a Keithly 503 milliohmmeter. Temperature and resistance were recorded simultaneously during the measurements. Tablets of dimensions 15 × 5 × about 2 mm were pressed from powder samples at a pressure of 5 tons. A sample holder with screw driven contacts constructed by Dr. R. de Jonge was used. The measurements were made in a N_2 atmosphere. Prior to measurement, the tablets were annealed in an evacuated quartz tube at 700°C.

Results

The DTA result indicated a small exothermic effect upon cooling and a similar endothermic effect upon heating with the peak positions of the exo- and endothermic effects differing by about 4°C. The total effect was spread over a temperature interval of about 60°C with the average of the heating and cooling peak positions at 630°C and the high-temperature limit of the thermal effect at approximately 650°C.

The variations of lattice parameters with temperature were determined by estimating the splitting of the lines 200 and 110, 201 and 111 and, in some cases, 310 and 020 to obtain the b/a ratio and by estimating the positions of the diffraction lines relative to their room temperature positions to obtain a and c. The room temperature values of the lattice parameters were determined by use of the diffractometer to be $a = 5.822 \pm 0.002$, $b = 3.305 \pm 0.001$, and $c = 5.859 \pm 0.0015$ Å. These values are in good agreement with the lattice parameters reported by Grønvold et al. (*7*) for $VS_{1.00}$. The variation of lattice parameters with temperature is shown in Fig. 1. The data demonstrate that the orthorhombic b axis increases more with temperature than does the a axis, and that $a/b = \sqrt{3}$ at about 575°C and higher temperatures.

The relative changes with temperature of the a and b axes are consistent with the observed relative changes of these axes with changing V/S at room temperature (*2*), in which case b increases and a decreases with decreasing V/S until $a/b = \sqrt{3}$. The temperature at which the transition is observed to be complete in the DTA experiment and the diffraction experiment differ by about 75°. Although the measurement of temperature in the Guinier experiment is unreliable relative to that in the DTA experiment for several reasons, it is unlikely that the discrepancy between the measured temperatures would be as large as 75° if the temperatures at which the thermal effects occurred and the long-range order of the MnP-type was lost were the same. It is more likely that the thermal effects are

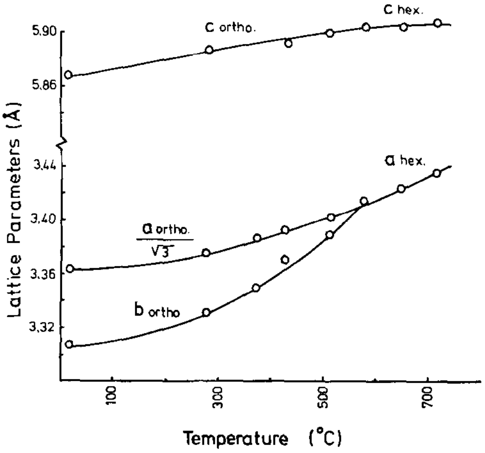

FIG. 1. Lattice parameters of VS vs temperature.

principally associated with the loss of short-range order and the diffraction effects with the loss of long-range order, and that long-range order of the MnP-type structure is lost at lower temperatures than the related short-range order.

The variation of electrical resistivity with temperature is shown in Fig. 2. It is probable that the sample was slightly oxidized during the course of the measurement, for a slight change of the color of the exterior of the pressed tablet was observed. When the sample was examined by X-ray diffraction after the resistivity measurements, only diffraction lines from VS were present in the powder pattern, indicating that oxidation was not excessive. Due to possible oxidation, and due to inherent uncertainties in the measurement of resistivity using pressed powders, the values of the resistivities determined are probably accurate only within an order of magnitude and in the direction of change with temperature. The measurements were made mainly upon heating, for an attempt to continue the measurements upon cooling from the highest temperature resulted in loss of contact. However, the contact was maintained over a sufficient temperature interval upon cooling to provide a clear indication that the resistivity was reversibly increasing with decreasing temperature at the high temperatures. Attempts to reproduce the measurements failed to yield high-temperature resistivities due to loss of contact and sample fracture. The measured room-temperature values did agree with that given in Fig. 2 to well within a factor of ten, and the resistivity clearly showed an increase with increasing temperature in the neighborhood of room-temperature in all cases. There was no measurable Hall effect indicating that the mobility of the electrons is less than 4 $cm^{-2}V^{-1}$ sec^{-1}.

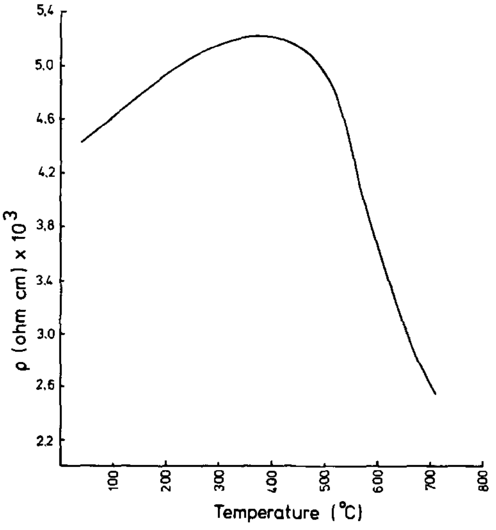

FIG. 2. Resistivity of VS vs temperature.

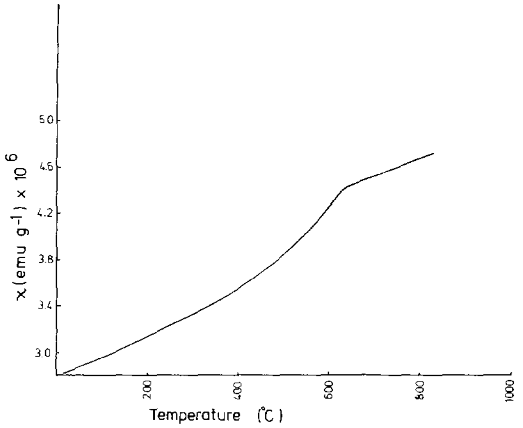

FIG. 3. Magnetic susceptibility of VS vs temperature.

The magnetic susceptibilities of VS are shown in Fig. 3. The uncertainties in the values given due to uncertainties in the measurements are calculated to be about $\pm 0.4 \times 10^{-6}$ emu g^{-1}, and all of the experimental points fall within these limits from the curve of Fig. 3. The room temperature value of 2.9×10^{-6} emu g^{-1} determined here is in good agreement with the values 2.5×10^{-6} and 3.1×10^{-6} emu g^{-1} determined for $VS_{0.975}$ and $VS_{1.10}$, respectively, by Grønvold et al. (*7*).

Discussion

The results of the experiments reported here, especially the DTA and X-ray results, tend to confirm the conclusion of prior studies (*2*, *3*) that the transition from NiAs-type to MnP-type in VS is essentially second order. The X-ray data show that the thermal expansion of VS is anisotropic, and that the principal anisotropy is in the rapid increase of the *b*-axis with temperature. The MnP-type distortion of the NiAs-type structure results in rows of V atoms in the configuration that is initially a plane hexagonal array, becoming alternatively closer and further apart resulting in the formation of zigzag chains of V atoms. The hexagonal symmetry is lost, and the *a* and *b* axes are free to vary independently, In principle this variation could result in either an increase or a decrease in a/b. The fact that *b* decreases more rapidly with decreasing temperature than does *a* means that the V–V distances within a given row are decreasing more rapidly than the distance between the zigzag chains. Thus two symmetrically inequivalent events that occur upon the distortion in VS both correspond to enhanced V–V interactions within chains as opposed to interactions between the chains.

The electrical conductivities of VS are of the order of magnitude expected for electronic conduction, and the increase in resistivity with increasing temperature at the lower temperatures is indicative of metallic behavior. The low mobility of the electrons is also characteristic of metals. Thus the decrease in resistivity with increasing temperature at temperatures above 400°C is most probably an electronic effect in a metallic solid, and is probably related to the other unusual features of solid VS in this temperature region.

The decrease in resistivity could be due to a rapid increase in the density of states at the Fermi energy. This would imply that the density of states at the Fermi energy in the NiAs-type is greater than in the MnP-type solid. However, since the decrease in resistivity initiates at temperatures significantly lower than the temperatures of the transition as determined by DTA or high-temperature Guinier diffraction, it would follow that the electronic effects are precursors of the change to higher symmetry.

The magnetic susceptibilities observed for VS are of the order of magnitude expected for Pauli paramagnetic substances. However, the increase in susceptibility with increasing temperature is not characteristic of free electron metals, and thus the susceptibility behavior, in agreement with the resistivity behavior, suggests an increasing density of states at the Fermi energy with increasing temperature, initiating at some temperature significantly below the transition temperature.

Conclusions

The properties of VS and the changes in properties through the MnP-type to NiAs-type phase transition indicate that the solid is metallic and that there is a change in the density of states of the conduction electrons that is associated with and that initiates prior to the transition to the NiAs-type structure. The formation of zigzag chains of vanadium atoms in (approximately) the *a*–*b* plane of the distorted solid suggests that the density of states effect is associated with the chain formation.

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