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Electric and Magnetic Properties of \(V_{x}Ti_{1-x}S\)^* 

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Abstract.— Electrical conductivity, magnetic susceptibility, and Hall voltage have been measured from 4 to 300 K on \(V_{x}Ti_{1-x}S\) (0 ≤ x < 0.10). \(T^2\) dependence in resistivity was observed for x < 0.02 with resistivity minima \(\rho \approx 20 K\) suggesting a local moment in agreement with magnetic susceptibility measurements. Crystals with 0.04 ≤ x < 0.10 exhibit semiconducting behavior with temperature dependent "band gap", we suggest Anderson localization of conduction electrons. Magnetic susceptibility data show Curie-type behavior corresponding to \(V^{3+}\) with ferrimagnetic ordering at low temperature. Anomalies in resistivity were observed at temperatures corresponding to ordering in the susceptibility.

Several studies /1,2/ have been carried out on \(Ti_{1+x}S_2\) to determine conditions for obtaining stoichiometric \(TiS_2\). \(TiS_2\) is complicated by possible existence of vacancies at titanium sites and interstitial titanium. All these studies have attempted to explain the discrepancy between the resistivity data (metallic behavior with \(T^2\) dependence) /1/, the photoemission work /3/, and the band structure calculation /4/ which gives an indirect gap of 0.2 - 0.3 eV. The present work was undertaken to investigate the effects of vanadium substitution.

Vanadium concentration was determined by neutron activation. Electrical conductivities and Hall effect were measured on single crystals by conventional methods. Magnetic susceptibility measurements were made using the Faraday method.

Room temperature values of \(\chi_m\) and \(\rho\) are linearly dependent on composition. Resistivity as a function of temperature is shown in figure 1. At low vanadium concentration, \(T^2\) dependence is observed with resistivity minima at 18 K and 22 K, respectively. At 3.7 % V there is practically no temperature dependence of \(\rho\) except for the anomaly at 30 K. The more heavily substituted crystals behave like semiconductors. These are not conventional semiconductors; the "band gap" diminishes with decrease in temperature. Anomalies were also observed at \(\approx 30 K\).

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Fig. 1: Resistivity as a function of temperature of \(V_{x}Ti_{1-x}S\).

The Hall constants in figure 2 show that the metallic samples are insensitive to variation in temperature. 8.0 % V and 6.2 % V show an increase with falling temperature, indicating decrease of the conduction electron density in the semiconducting crystals. For 3.7 % V, the anomaly in the resistivity can be seen as partially due to sudden increase in the conduction electron concentration.

In figure 3, the samples show Curie-type behavior with 2.8 \(\mu_B\) per mole of vanadium suggesting \(V^{3+}\) (\(d^2\)). At low temperature (< 30 K), ferrimagnetic ordering sets in. It decreases abruptly the electron phonon scattering and hence causes the observed anomalies in resistivity.
There are two existing band models for TiS₂. The semimetallic model of Thompson /1/, Kukkonen and Maldague /5/, attributes the $T^2$ dependence of resistivity to electron hole scattering. In this model, the p and b bands are very close to each other or even overlap. According to Kukkonen and Maldague, the presence of 0.39% excess Ti ($\sim 10^{22}$) there is a substantial deviation from $T^2$ dependence. With 1.4% V the change in electron concentration ($\sim 2 \times 10^{22}$, assuming $V^{+3}$) is great enough to cause deviation from the $T^2$ dependence. Wilson /6/, in his dirty semiconductor model, attributes the $T^2$ resistivity dependence to electron scattering by "Fivaz mode" /7/ optic homopolar phonons, an $A_{1g}$ vibration in the case of TiS₂. With the "Fivaz mode", primarily due to lattice disorder, the carrier mobility was derived as $\mu T^{-n}$ where $n$ depends solely on the energy of the $A_{1g}$ mode ($n = 2$ for TiS₂). In a Raman study of HfS₂, ZrS₂ and TiS₂, Smith et al. /8/ observed that the energy of the $A_{1g}$ mode is independent of the metal ion. Hence, the replacement of Ti by V should not alter the energy of the $A_{1g}$ mode, and consequently, the temperature dependence of the mobility. With the observed temperature-independent Hall constant for the slightly doped samples, the resistivity should obey the same $T^2$ laws as in TiS₂, which was indeed the observed case. Recent work by Friend et al. /9/ on the pressure dependence of resistivity and Hall constant of TiS₂ and TiSe₂ crystals is in agreement with the extrinsic semiconductor model.

For higher vanadium concentrations ($\kappa > 0.04$) the crystal exhibit semiconducting behavior with a varying "band gap". We suggest Anderson localization of conduction electrons due to potential fluctuations created by randomly distributed vanadium ions. The effect, however, is complicated by ferrimagnetic interaction between the vanadium ions.

References


Fig. 2: Hall constant as a function of temperature of $V_{x}Ti_{1-x}S_{2}$.

Fig. 3: Reciprocal molar susceptibility (diamagnetically corrected $\sim 70 \times 10^{-6}$ c.g.s. mole$^{-1}$) as a function of temperature of $V_{x}Ti_{1-x}S_{2}$.