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Anomalous Electrical and Magnetic Properties of Vanadium Diselenide*

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Powder samples of VSe_2 have been made by direct synthesis from the elements. Single-crystal specimens have been made by vapor phase transport in the presence of iodine. X-Ray characterization indicated only the 1*T* polytype. Behavior was metallic over the range 1.5 to 300°K, but there were discontinuities at about 100°K in resistivity, magnetic susceptibility, and Hall voltage. These are apparently due to the onset of charge density waves. Below 50°K, there was a clear quadratic dependence of resistivity on temperature which combined with relatively high Pauli paramagnetism to indicate Baber-type electron–electron scattering. No superconductivity was observed down to 1.5°K.

Introduction

In the course of an extended investigation into the influence on structure and properties of partially substituting vanadium for niobium in the layered compound niobium diselenide (*1*, *2*), we had occasion to prepare the end member ($x = 1$) of the series $Nb_{1-x}V_xSe_2$ for a comparison of its electrical and magnetic properties. VSe_2 is a layered compound in which the sheet of vanadium atoms occupies octahedral holes between two sheets of hexagonal-packed selenium atoms. Its physical properties are unusual but relatively little information on it has appeared in the literature. Hoschek and Klemm (*3*), who were apparently the first to make it, as $VSe_{1.62-1.97}$, determined the structure to be of the $Cd(OH)_2$ type (Fig. 1) and found by magnetic measurements at 20 and −183°C that the paramagnetic susceptibility rapidly decreased to near zero as the selenium:vanadium ratio approached 2:1. Subsequently, Røst and Gjertsen (*4*) extended the magnetic investigation over a broader temperature interval (90–700°K) and reported for both $VSe_{1.96}$ and $VSe_{2.05}$ a small, practically temperature-independent paramagnetism with a barely perceptible maximum at 195°K. Wilson and Yoffe, in their comprehensive review of transition metal dichalcogenides (*5*), presented a fragment of the transmission spectrum at 77°K for VSe_2 (essentially featureless in the interval 15,000–30,000 cm^{-1}) but gave no details of its preparation or other properties. Most recently, Thompson and Silbernagel (*6*) reported to the American Physical Society on the charge density wave transition in VSe_2, but again no details are available. In this communication, we describe the preparation, chemical analysis, and magnetic and transport properties of vanadium diselenide.

Experimental

The samples were prepared by allowing the elements (99.98% vanadium wire from Leico Industries and 99.999% selenium shot from Alfa Inorganics) in stoichiometric amounts to react in evacuated silica tubes. The tubes were heated at 15°/hr to 750°C and then held at temperature for 8 days. The samples were opened in a nitrogen-filled dry box, ground in

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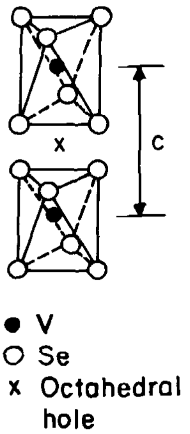

Fig. 1. Structural arrangement in VSe_2. The polytype is $1T$. All the VSe_2 layers are identical.

an agate mortar, resealed in silica tubes, and refired for 8 days at 750°C. During each firing, the silica tubes were contained in metallic coils (Kanthal) in order to avoid any temperature gradient along the tube. It was observed that without the coil, a small amount of selenium condensed on the walls of the tube during the cooling process. All lines in the X-ray diffraction patterns of the products were indexed on the basis of a hexagonal unit cell. The lattice parameters, obtained from back diffraction using a Debye–Scherrer camera of nominal diameter 114.6 mm and Cu$K\alpha$ radiation, are compared in Table I with the values of Røst and Gjertsen for $VSe_{1.96}$ and $VSe_{2.05}$.

Single crystals of VSe_2 ($1 \times 2 \times 0.1$ mm^3) were prepared by chemical transport using a concentration of 1 mg/cm^3 of iodine as transporting agent (*7*). At the start of the transport run, the charge end was kept at 120°C, the other end at 810°C, and the center growth zone at 780°C. Such an arrangement minimizes the number of nuclei in the growth zone. After 24 hr, the charge zone was raised to 800°C, the other end maintained at 810°C, and the center zone programmed to 734°C at the rate of 1°/hr. Transport was allowed to continue for 10 days after the growth zone reached the desired temperature. All the heaters were then shut off and the tube was allowed to cool to room temperature. The crystals were removed from the transport tube by snapping it in an evacuated transparent plastic hose. Crystals were freed of excess iodine by heating at 150°C under vacuum using a liquid nitrogen trap.

TABLE I

Lattice Parameters of Vanadium Diselenide

Sample	a (Å)	c (Å)
This work	3.356 ± 0.001	6.105 ± 0.002
$VSe_{1.96}$ (*5*)	3.353	6.101
$VSe_{2.05}$ (*5*)	3.356	6.104

Chemical analysis was done by igniting the selenide in a stream of dry oxygen to V_2O_5. Since V_2O_5 has a marked tendency to be slightly oxygen deficient, an apparent excess in selenium should be observed. The formula found was $VSe_{1.995}$.

Magnetic susceptibilities were measured over the range 1.6–300°K using the Faraday method with Spectrosil quartz buckets and Cahn Electrobalance force recording as described in (*8*). The temperature was monitored by a calibrated germanium resistance thermometer (1.5–100°K) and a copper–constantan thermocouple calibrated against a gallium–arsenide diode (100–300°K). Susceptibility measurements, which were field independent, were corrected for the diamagnetism of the quartz bucket and are believed to be accurate within 1%.

For the measurements of resistivity (perpendicular to the c-axis) the Hall coefficient (magnetic field parallel to c, Hall voltage measured perpendicular to c), five copper probes were connected with silver paint to the flat single crystal. It was found that silver contacts were stronger and better conducting than ultrasonically soldered indium. Apparently ultrasonic soldering creates mechanical distortions at the contacts, which may be particularly bad for layer compounds. An ac setup (400 Hz) using a misalignment resistor and lock-in amplifier was used to measure the Hall voltage. The upper limit of the sensitivity of the apparatus was determined by the noise and was of the order of 5 nV. Linear proportionality to magnetic field (0–6 kG) and to ac current (0–50 mA) was verified. The dc resistivity was measured by the conventional van der Pauw technique. Ohmic behavior was observed throughout. An uncertainty of about 5% can be attributed to the Hall voltage and resistivity results.

Results and Discussion

As shown in Fig. 2, our VSe_2 samples showed metallic behavior from 300 to 1.5°K. No transition to a superconducting state was observed. Around 80°K there was an anomaly in the evolution of resistivity as a function of temperature. Similar anomalies were observed to occur at slightly higher temperatures in the magnetic susceptibility (Fig. 3) and the Hall coefficient (Fig. 4). The results are roughly in agreement with those previously reported (*4*, *6*). However, we find a magnetic susceptibility about 30% lower than the value suggested by reference (*6*), a Curie-type behavior at much lower temperatures, and a Curie constant that is much smaller.

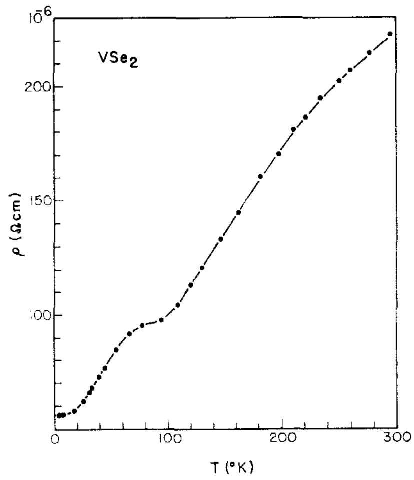

FIG. 2. Electrical resistivity as a function of temperature for a single crystal of 1*T*-VSe_2.

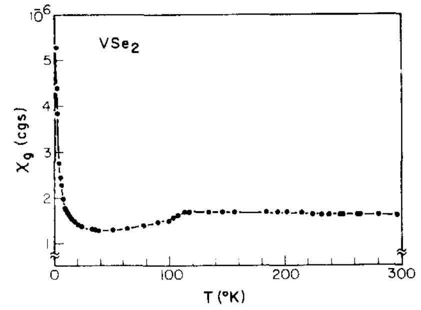

FIG. 3. Observed per-gram magnetic susceptibility as a function of temperature for powder VSe_2.

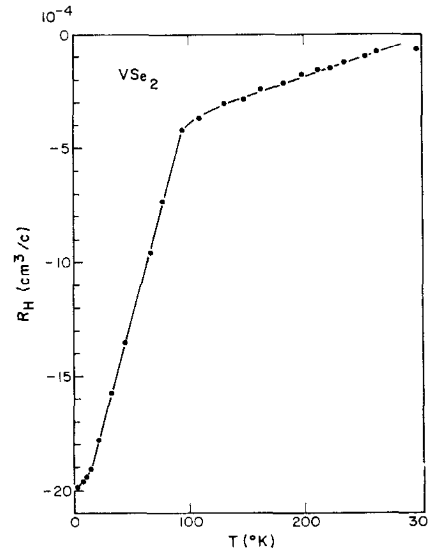

FIG. 4. Hall-voltage constant as a function of temperature for a single-crystal specimen of 1*T*-VSe_2.

The net paramagnetic susceptibility of VSe_2 is very high for a metal; at room temperature, having subtracted from the observed susceptibility, a core diamagnetism of -102.9×10^{-6} emu/mole (*9*), we find $+437 \times 10^{-6}$ emu/mole. Two contributions to this value are to be expected: the Pauli electron-gas susceptibility and Van Vleck paramagnetism arising from excited states. For dioxides and dichalcogenides of the transition metals, the Van Vleck paramagnetism is usually no greater than 100×10^{-6} emu/mole. The Pauli paramagnetism should be of approximately the same order. With $m^* \approx 2m_0$, the Pauli–Peierls equation

$$\chi = \frac{4\pi m^*}{h^2}\left(\frac{3n}{\pi}\right)^{1/2} \mu^2{}_B \left[1 - \frac{1}{3}\left(\frac{m_0}{m^*}\right)^2\right] \frac{MW}{\rho}$$

(where n is the number of conduction electrons per unit volume, m_0 and m^* are the electronic rest and effective masses, h is the Planck constant, μ_B is the Bohr magneton, MW is the molecular weight, and ρ is the density) gives a value of 37 × 10^{-6} emu/mole. Thus we have approximately 300 × 10^{-6} emu/mole unaccounted for.

Below 40°K, the susceptibility seems to increase in a Curie-type manner (Fig. 3). Figure 5 shows as a function of temperature the inverse of

$$\Delta\chi_M = \chi_{M(\text{observed})} - \chi_{M(\text{background})},$$

where $\chi_{M(\text{background})}$ is the temperature-independent contribution to the paramagnetism. The latter value is not known, but it can be estimated from the minimum in Fig. 3 as 1.27 × 10^{-6} emu/g or 265 × 10^{-6} emu/mole. Figure 5 shows $(\Delta\chi_M)^{-1}$ vs T for three possible choices of $\chi_{M(\text{background})}$: 200, 265, and 335 × 10^{-6} emu/mole. Assuming a Curie dependence, it is seen that 200 × 10^{-6} emu/mole gives the best fit. The corresponding Curie constant would be 7.5 × 10^{-6} emu/deg/mole. It is believed most likely that the Curie behavior stems from V^{4+} in the van der Waals gap between the VSe_2 layers (i.e., the octahedral holes marked X in Fig. 1), acting as localized paramagnetic centers. The observed value of C_M would correspond to 2 × 10^{-5} mole of V^{4+} per mole of VSe_2. An interesting alternate possibility is that the dependence of the excess paramagnetism is Curie–Weiss, in which case the points marked (b), derived from the actually observed minimum, represent a better fit. In such case, there would be a positive Weiss constant, implying ferromagnetic ordering of the interlayer V^{4+} moments. This may be connected with the nonappearance of superconductivity in VSe_2.

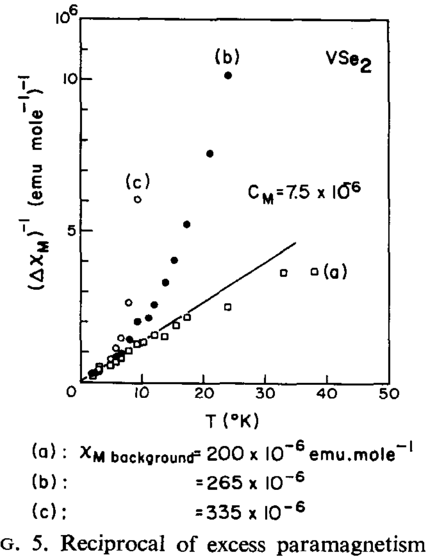

FIG. 5. Reciprocal of excess paramagnetism over background as a function of temperature. The straight line gives the best Curie fit. The points marked (b) correspond to a background estimate based on the minimum in the curve of Fig. 3.

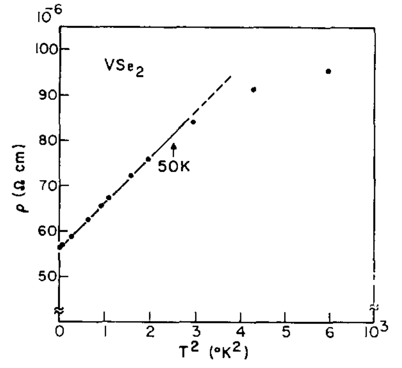

FIG. 6. Electrical resistivity as a function of squared temperature for a single-crystal specimen of 1T-VSe_2.

Between 105 and 110°K, there is a slope discontinuity in the magnetic susceptibility (Fig. 3). This should probably be related to the appearance of a charge density wave (CDW), as recently suggested by Wilson (*10*). The CDW is probably also associated with the anomaly in the resistivity around 100°K (Fig. 2) and the sharp increase of $|R_H|$ below the same temperature (Fig. 4). On a one-carrier model, the increase of $|R_H|$ would correspond to a decrease in carrier concentration associated with the onset of CDW.

An interesting feature of the resistivity as a function of temperature is the quadratic dependence observed below 50°K (Fig. 6). Such behavior was predicted by Baber and Wills (*11*) for a multivalent metal in which strong scattering comes from collisions between electrons. McWhan and Rice (*12*) observed T^2 dependence of the resistivity in V_2O_3 under high pressure. For VSe_2, if we write $\rho = \rho_0 + BT^2$, we find a very large B value of 0.01 $\mu\Omega$ cm/deg^2, which is about 10^3 times the typical value for transition metals but comparable to that found in V_2O_3. As pointed out by Baber and Wills (*11*), the condition for large T^2 contribution to the resistivity is that the effective mass of the conduction electrons be large, leading to high paramagnetism. Such a situation seems to correspond to our results.

Addendum. After this manuscript had been completed, it was learned that van Bruggen and Haas (*13*) have recently investigated the magnetic susceptibility and electrical properties of VSe_2 single crystals and have found results that are in essential agreement with those reported here.

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