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Resistivity, Magnetoresistance, and Hall Effect Studies in $VO_x(0.82 \leq x \leq 1.0)$*‡

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Resistivity (ρ), magnetoresistance ($\Delta\rho/\rho_0$), and Hall coefficient (R) measurements were carried out on annealed, polycrystalline, single phase VO_x ($0.82 \leq x \leq 1.0$) samples at $T = 4.2$, 77, 300°K. These samples did not undergo a semiconductor–metal transition; they had room temperature resistivities in the range $10^{-3} > \rho > 10^{-4}$ Ω cm, small negative values of $d\rho/dT$, small Hall coefficients $R \sim 5 \times 10^{-4}$ cm^3/C, and positive values of $\Delta\rho/\rho_0$ at 4.2°K. An overlapping band structure model is proposed to explain these and comparable observations in the literature.

Introduction

As part of a continuing series of investigations we report here the results of resistivity, magnetoresistance, and Hall measurements on $VO_x(0.82 \leq x \leq 1.0)$ at 4.2, 77, and 300°K. Early resistance measurements by Morin (*1*) and Austin (*2*) indicated that VO was metallic for $T \gtrsim 126$°K and a semiconductor for $T \lesssim 126$°K. Additional evidence for a metal–semiconductor transition was provided by Warren et al. (*3*). However, other work failed to confirm these findings; sintered pellets (*4–6*) as well as single crystal films (*7*) were reported to be metallic between 77 and 300°K. In two review articles, Adler (*8*) supported the view that VO does undergo a transition though he did not rule out the opposite alternative. Among other matters he suggested that random impurities or departures from stoichiometry might have depressed the transition temperature sufficiently for the transition to have been missed by those investigators who did not report it.

In an extensive, systematic investigation (*9*) on approximately thirty well-characterized samples of known composition covering the entire homogeneity range ($0.75 \leq x \leq 1.30$), no semiconductor-metal transition was observed between 77 and 300°K for any sample. The data indicate that metal-rich VO_x exhibits metallic behavior, whereas near the oxygen-rich end of the homogeneity range VO_x is a semiconductor. It seemed desirable to use the same samples to extend the resisitivity measurements to 4.2°K and to determine Hall coefficients and magnetoresistivities for the first time. In this paper we report results on metal-rich samples ($0.82 \leq x \leq 1.0$); it is planned to extend these measurements into the oxygen-rich stoichiometry region.

Experimental

VO_x with $0.82 < x < 1.01$ was prepared by mixing pure vanadium metal with appropriate amounts of V_2O_5 and arc melting these under gettered argon. The molten product was subsequently quenched by casting it in a graphite cylinder, and then annealed in vacuum at 1300°C, according to a procedure detailed elsewhere (*10*). Only material that was found to be single phase under X-ray and metallographic examination, as well as homogeneous and free from cracks, was used. The composition of each sample was ascertained by monitoring the mass gain in a careful oxidation of aliquot portions to V_2O_5. Mass spectrographic examination showed the following principal impurities: Ni–70, Fe–120, Ca–190, P–120, Si–400, Al–200, Mg–80, all others < 40

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ppmA. Microcombustion and micro-Kjeldahl tests established the C and N impurity content at 100 and 130 ppmA, respectively.

Measurements of ρ_0, R, and $\Delta\rho/\rho_0$ were carried out by standard 4-probe techniques, using a commercial digital voltage–frequency converter to monitor the very small signals observed with input currents in the 10–300 mA range. Averages were taken over time intervals sufficiently long to achieve the desired sensitivity. Hall and magnetoresistance measurements were carried out at the Francis Bitter National Magnet Laboratory at MIT in fields up to 210 kG, with appropriate precautions involving magnetic field and input current reversals.

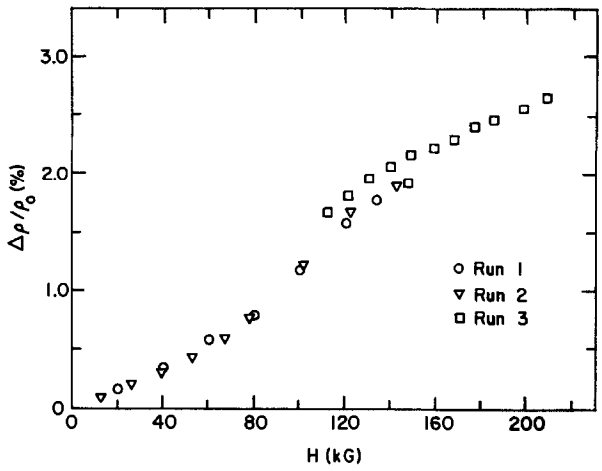

FIG. 1. Magnetoresistance for $VO_{0.88}$ at 4.2°K.

Results

The resistivities (ρ), Hall coefficients (R), and magnetoresistances ($\Delta\rho/\rho_0$) of several VO_x samples are listed in Table I. The following points are noteworthy:

1. In the composition range $0.82 \leq x \leq 1.0$ the resistivity does not change by more than a factor of four between 4.2 and 300°K. This finding invalidates the hypothesis that a metal-to-semiconductor transition occurs in VO of fixed composition, but is frequently depressed below 77°K due to impurities or departures from stoichiometry.

2. The temperature coefficient of resistivity is negative over the temperature and composition range under study; this extends earlier findings into the liquid He temperature region. Examination of Table I also confirms the observation (*9*) that $d\rho/dT$ is negative, small, and relatively insensitive to x.

3. The Hall coefficient is very small: $|R| < 8.6 \times 10^{-4}$ cm^3/C under all conditions examined here; on a one-band model this corresponds to charge carrier densities $n > 7.2 \times 10^{21}$ cm^{-3}. R varies only very slightly with magnetic field and is negative. This latter observation should be viewed with caution, however, since the Hall signal had to be extracted from Hall misalignment and anisotropic magnetoresistance signals, both of which exceeded the Hall voltage by four orders of magnitude. The fact that R is very small at 4.2°K is also consistent with the fact that VO_x is a metal for the stoichiometry range studied here.

4. At 77 and 300°K, $\Delta\rho/\rho_0$ was smaller than the experimental error of ± 0.01 % for all samples. The results of several magnetoresistance runs on $VO_{0.88}$ at 4.2°K are depicted in Fig. 1 as a function of magnetic field, H. There is an initial near-parabolic rise of $\Delta\rho/\rho_0$ with H, followed by a changeover to a linear dependence on field above 120 kG. As shown in Table I, except for the stoichiometric sample, the transverse magnetoresistance at 150 kG is in the range of 1–2%.

Discussion

The above findings and similar results described elsewhere (*4*, *7*, *9*) may be explained by an overlapping band model in which the Fermi surface

TABLE I

ELECTRICAL PROPERTIES OF VO_x

	$\rho_0 \times 10^4$ (Ωcm)			$R \times 10^4$ (cm^3/C) at 150 kG			$\Delta\rho/\rho_0$ at 150 kG (%)
x	4.2°K	77°K	300°K	4.2°K	77°K	300°K	4.2°K
0.82	8.4	8.3	7.1	−5.9	−6.9	−6.6	0.6, 1.3
0.83	8.7	7.5	6.3	−5.8	−8.6	−6.2	1.5, 1.8
0.88	8.8	8.3	7.5	—	−4.6	—	2.0, 2.1, 2.2
1.00	63	37	19	2.1	—	—	0.4

cuts through several bands at once. Such a model receives indirect support from the magnetoresistance data as well as from recent calculations by Ern and Switendick (*11*). The observed positive $\Delta\rho/\rho_0$ values exceed by several orders of magnitude the values predicted (*12*) for highly degenerate ($n \sim 10^{22}$ cm^{-3}) conductors characterized by a single band of standard form. However, the measurements are consistent with a model in which electrons and holes located in several overlapping bands participate simultaneously in conduction processes. It may be shown (*12–14*) that for intrinsic samples $\Delta\rho/\rho_0$ increases as H^2 without limit; with successively greater departures of $|n-p|$ from zero, $\Delta\rho/\rho_0$ deviates from the quadratic field dependence and saturates at successively lower values of the magnetoresistance. Analysis of the data in Fig. 1 according to the method proposed elsewhere (*15*), which assumes mirror image bands, gives the carrier mobilities of approximately 10^2 cm^2/V sec at 4.2°K.

Ern and Switendick (*11*) applied the APW method to determine the band structure of idealized TiC, TiN, and TiO without considering vacancies. Since VO has the same crystal symmetry, the results for TiO should carry over to the present case. However, with the smaller radial extent of the cationic wave functions, the bands in VO should be considerably narrower than those calculated for TiO; also, with changes in the atomic potentials, the relative positions of the various bands will be altered. The net effect should be to introduce a larger gap between the predominantly anionic band of *p*-type symmetry and the predominantly cationic band of *s-d* type symmetry than is shown for TiO in Figs. 5 and 7 of Ref. (*11*). In this sense, we support Goodenough's contention (*7*) that the properties of VO should be interpretable in terms of a density-of-states curve with very pronounced bimodal characteristics.

If one were to adopt the band structure and the density-of-states histogram for TiO (*11*) without any change, the Fermi level for $VO_{1.0}$ would coincide very nearly with that of $TiO_{0.80}$ at $\zeta \approx 0.74$ Ry, and the Fermi level for $VO_{0.82}$ would fall at $\zeta \approx 0.78$ Ry. This shift is sufficient to cause drastic alterations in the contours of the bands being intersected by the Fermi level. On observing the loci of the intersections as the Fermi level is raised through 0.17 Ry in Fig. 5 of Ref. (*11*), corresponding to the homogeneity range $1.30 \geqslant x \geqslant 0.75$, one concludes that samples for which $x \gtrsim 0.9$ should involve *n*-type carriers in significantly higher concentrations than samples for which $x \lesssim 1.0$. These conclusions are buttressed by the observation that in the range $0.75 \leqslant x \leqslant 1.0$ the Fermi level ($0.80 \geqslant \zeta \geqslant 0.74$) falls on a part of the density-of-states curve for TiO with positive slope, whereas for $1.0 \leqslant x \leqslant 1.35$ the Fermi level ($0.74 \geqslant \zeta \geqslant 0.63$) falls on a part of the density-of-states curve for TiO with negative slope.

It is clearly dangerous to rely too heavily on an analogy which involves use of the density-of-states curve for TiO to interpret the VO_x results. In particular, no allowance has been made for the presence of cationic and anionic vacancies or for any correlation effects among the carriers. In any realistic interpretation these matters must be taken into consideration. It is nevertheless proposed here that similar conclusions might be reached if a realistic band structure for VO were available. That is, the increase in occupancy of the *s-d* type band of VO_x caused by changes in stoichiometry (8% of band capacity when x is altered from 1.0 to 0.82) is presumed to result in a drastic imbalance between groups of positive and negative carriers.

If the above conclusion is accepted, the various experimental observations may be interpreted on a reasonably straightforward basis. First, VO_x with $0.82 \leqslant x \leqslant 1.0$ is expected to be metallic unless spontaneous crystallographic distortions or magnetic ordering processes create subbands separated by gaps within which the Fermi level falls. There is no evidence in our study ($x \leqslant 1$) for the formation of subbands. From the earlier work (*9*) it may be concluded, however, that for $x > 1$ the Fermi level is depressed into an energy range where a gap is encountered. In the corresponding composition range VO_x exhibits semiconducting properties; however, no semiconductor-metal transition is observed.

A second conclusion reached on the basis of the above model is that both Hall and Seebeck coefficients should remain numerically small and may be expected to change sign with changes in stoichiometry. This is because the one-band effects combine to yield an overall Seebeck or Hall coefficient according to the relations (*12, 14*)

$$\alpha = \sum_j \sigma_j \alpha_j / \sigma$$

and

$$\mathrm{R} = \sum_j \mathrm{R}_j \sigma_j^2 / \sigma^2 \text{ (low field limit)},$$

where $\sigma_j = n_j e u_j$, $\alpha_j \approx \pi^2 k^2 T / 3e\zeta$, and $R_j \approx (n_j e c)^{-1}$ are the one-band conductivities, Seebeck and Hall coefficients respectively; α_j and R_j are positive or negative according to the sign of the carriers in the *j*-th band. With the Fermi level cutting through many narrow bands, the various α_j and R_j and the carrier

mobilities u_j are expected to be small. The overall sign of α and R thus depends on the delicate balance between the positive and negative contributions weighted by the respective mobilities. With the present model, the electron effects can be expected to outweigh the influence of holes for low x and vice versa for high x; this accords with the observed sign changes in α (*6*, *9*) and R near $x = 1$. The model also shows why one would anticipate $|n - p|$ to be small and $\Delta\rho/\rho_0$ to be large in the range $x \gtrsim 0.9$.

Finally, it is possible to explain the observation that $d\rho/dT < 0$ for metallic VO_x. If this material follows the usual trend, according to which the various bands widen with rising temperature, then the degree of overlap is correspondingly increased. There is a concomitant increase in carrier densities; if this increase outweighs the decrease in carrier mobility with rising temperature, $d\rho/dT$ is negative.

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