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Transport properties of tungsten-doped VO_2

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Measurements of DC and AC conductivity and thermopower show that $VO_2:W$ can be treated as a conventional n-type extrinsic semiconductor with a donor level 0.06–0.08 eV below the conduction band. For samples with an impurity content from 0.67 → 1.70 at.% W, an effective mass ratio m^*/m of 65 ± 10 and a compensation ratio of 0.7 ± 0.1 are deduced from conventional semiconductor theory assuming donor exhaustion just below the metal semiconductor transition.

Des mesures de la conductivité CC et CA, ainsi que du pouvoir thermoélectrique, montrent que $VO_2:W$ peut être traité comme un semi-conducteur extrinséque ordinaire de type n possédant un niveau donneur situé à 0.06–0.08 eV au-dessous de la bande de conduction. Pour des échantillons ayant un contenu d'impureté allant de 0.67 à 1.70% d'at. de W, la théorie ordinaire des semi-conducteurs permet de déduire un rapport de masses de 65 ± 10 et un rapport de compensation de 0.7 ± 0.1, en supposant qu'il y a épuisement du niveau donneur juste au-dessous de la transition de l'état semi-conducteur à l'état métallique.

[Traduit par le journal]

Can. J. Phys., **54**, 408 (1976)

1. Introduction

The addition of tungsten impurity atoms to vanadium dioxide (VO_2) causes the metal–semiconductor transition to occur at lower temperatures than the 67 °C found in undoped crystals, increases the conductivity in the semiconducting phase, and also reduces the activation energy for conduction in this phase from 0.5 eV to between 0.05 to 0.08 eV (Nygren and Israelsson 1969; Reyes *et al.* 1972; Horlin *et al.* 1973; Kleinschmidt 1974). This differs from the effects of impurities such as Al and Cr which have relatively little effect on the conductivity in the semiconducting phase (Reyes *et al.* 1975, 1976*a*; Reyes 1974), and it has been suggested that tungsten acts by the formation of donor states located 0.05 eV to 0.08 eV below the conduction band (Reyes *et al.* 1972). In this paper, we show that all the transport properties are compatible with this interpretation, and we obtain a direct estimate of the effective mass of carriers in the conduction band by the application of conventional semiconductor theory. The value obtained of $m^*/m = 65 \pm 10$ agrees with that proposed by Zylbersztejn and Mott (1975) on the basis of magnetic susceptibility measurements in $VO_2:Nb$.

2. Experimental

VO_2 crystals doped with differing amounts of W impurity atoms were prepared using an isothermal flux evaporation method with the dopant being added to the starting material. Details of the growth procedures have been given elsewhere (Reyes *et al.* 1972). The tungsten content was determined by a spectrographic technique and crystals were prepared with a composition of 0.31 to 1.70 at.% W.

3. Results

3.1 Conductivity

The electrical conductivity of VO_2–W single crystals is shown in Fig. 1. The two immediate observations of the effects of increasing tungsten content are a decrease in the temperature of the metal–semiconductor transition by −21 K/at.% W as reported previously (Reyes *et al.* 1972), and an increase in the conductivity in the semiconducting phase. This is mainly responsible for the smaller discontinuity, $\log_{10}(\sigma_m/\sigma_s)$ at the transition. Just below the transition temperature T_t, the activation energies (E_{a1}) are small and of the order of 0.05 eV. As the temperature is decreased, the activation energy increases, reaching a maximum (E_{a2}) at about 200 K. Further lowering of the temperature reduces the activation energy to E_{a3} at 80 K. A similar behavior was obtained by Kleinschmidt (1974) at lower tungsten concentrations.

Above T_t, three samples with different W concentrations exhibited positive temperature coefficients of resistance of the same order of magnitude as the pure material. In curves (a) and (b), this

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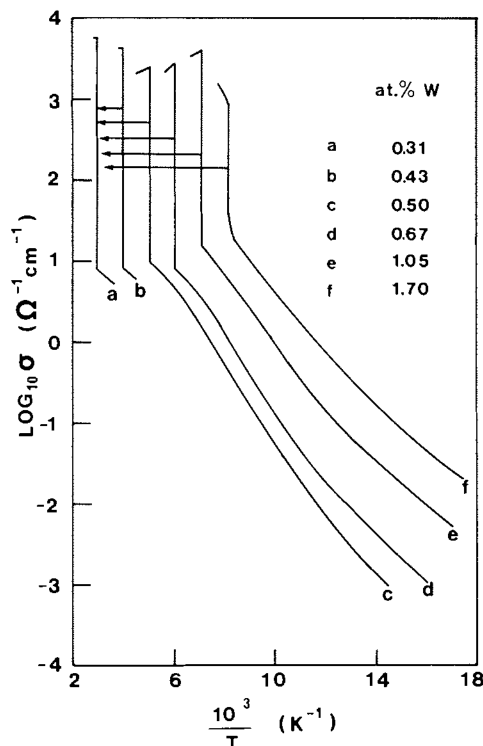

FIG. 1. Temperature dependence of the DC conductivity of VO_2 doped with W. The curves a, b, c, d, e, and f are displaced along the $10^3/T$ by one unit relative to each other. The actual positions are indicated by the arrows.

coefficient was not detectable over the range of temperatures covered in the experiments. Curve (f) did not show a metallic conductivity at all, but this was attributed to an inhomogeneous distribution of tungsten in the material, as shown by the wide temperature range over which the transition took place.

3.2 Band Properties

Conduction may occur in materials such as VO_2 either by band conduction or by hopping. As discussed elsewhere (Zylbersztejn and Mott 1975; Sayer *et al.* 1975) a distinction may be made between these processes on the basis of the observation of a frequency dependent AC conductivity and the temperature variation of the thermopower.

The AC conductivity measurements were made over a frequency range of 10^2–10^5 Hz and a temperature range of 20–340 K. No dispersion was observed between 77 K and 340 K, and a barely perceptible effect was noted only near 20 K. This differs from the strong frequency dependence observed in Al or Cr-doped crystals over the entire temperature range (Kabashima *et al.* 1972; Reyes *et al.* 1976*b*) and strongly suggests that conduction in VO_2–W occurs by a frequency independent band mechanism (Mott and Davis 1971).

The temperature dependence of the thermopower in VO_2 having different W contents is shown in Fig. 2. At high tempertaures, the thermopower is small and generally decreases with decreasing temperature. Such behavior is characteristic of a metal. A rapid rise in the thermopower is observed at temperatures which correspond with the cooling transition temperature found in DC conductivity. The temperature range over which the transition takes place is a measure of the temperature difference across the sample. Below the transition temperature T_t, the thermopower increases with decreasing temperature as expected for a semiconductor. For many extrinsic semiconductors, the thermopower is expected to vary according to the expression

$$[1] \quad S = -\frac{k}{e}\left\{\frac{(E_c - E_F)_0}{kT} - \frac{\gamma}{k} + A\right\}$$

where A is a term depending on the scattering

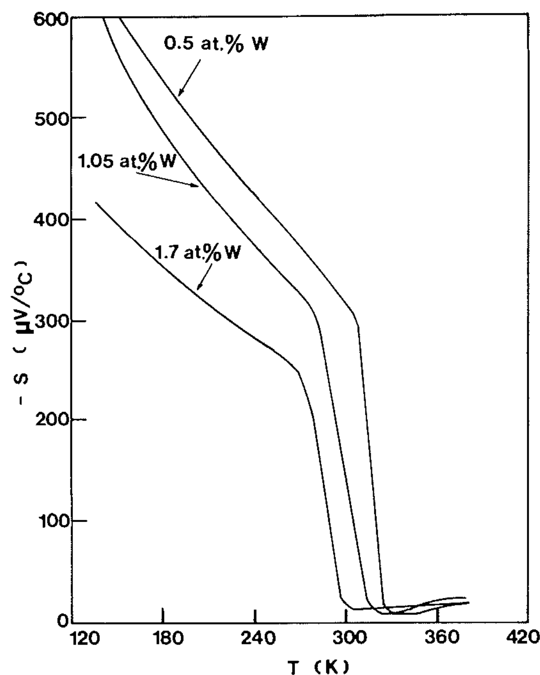

FIG. 2. Temperature dependence of the thermoelectric power (S) of tungsten-doped VO_2. The measurements were taken during cooling and the steep rise of S corresponds to the cooling metal-to-semiconductor transition.

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TABLE 1. Summary of the electrical properties of VO_2:W

W content	at.% W	0.31	0.43	0.50	0.67	1.05	1.70
Heating T_t	T_t^H(K)	333	331	327	325	320	304
Cooling T_t	T_t^C(K)	332	328	324	323	317	301
Conductivity change at T_t	$\log_{10}(\sigma_m/\sigma_s)$	2.8	2.7	2.4	2.5	2.3	1.7
Conductivity activation energies	E_{a1} (eV)	0.054	0.057	0.055	0.050	0.058	—
	E_{a2} (eV)	—	—	0.11	0.10	0.10	0.079
	E_{a3} (eV)	—	—	0.071	0.063	0.053	0.053
Donor energy	E_d (eV)	—	—	0.077	0.084	0.069	0.06
Thermopower	$E_{c0} - E_F$ (eV)	—	—	0.061	—	0.071	0.045
Scattering factor	A			5.6	—	4.5	4.0
Effective mass	m^*/m	—	—	28	85	57	63
Compensation ratio	κ	—	—	0.27	0.76	0.59	0.70

mechanism; $A = 2$ if phonon scattering is predominant, $A = 4$ if scattering occurs from ionized impurities. The parameter γ arises from the assumption that $(E_c - E_F)$ varies linearly with temperature such that

$$(E_c - E_F) = (E_c - E_F)_0 - \gamma T$$

where $(E_c - E_F)_0$ is the extrapolated value of $(E_c - E_F)$ at $T = 0$ (Blakemore 1962; Mott and Davis 1971). An independent value of γ can be estimated from the temperature dependence of the optical band gap $E_g = E_{g0} - \beta T$, since to a first approximation, if the temperature variation of E_c and E_V are equal and opposite, $\beta \sim 2\gamma$. For VO_2, $\beta = 600$ μeV/K (Ladd and Paul 1969) so that $\gamma = 300$ μeV/K.

A plot of S vs. $10^3/T$ below T_t is shown in Fig. 3. There is considerable curvature at high temperature, particularly for lightly-doped samples, but the low temperature behavior is reasonably linear. The overall behavior is summarized in Table 1, and in general it is seen that the values of $(E_c - E_F)_0$ are in good agreement with the activation energies deduced from conductivity data. To the accuracy justified by the experiment, and by the approximation $\beta = 2\gamma$, $A \simeq 4$, and it may be concluded that the dominant scattering mechanism is by ionized impurities.

In conclusion, the direct transport properties of VO_2:W are consistent with a band scheme with the impurity ions giving rise to extrinsic conduction from donor states.

4. Discussion

In order to substantiate this conclusion it is necessary to account for the complex temperature dependence of the conductivity in the semiconducting phase. This may be done using conventional theory for extrinsic conduction (Blakemore 1962).

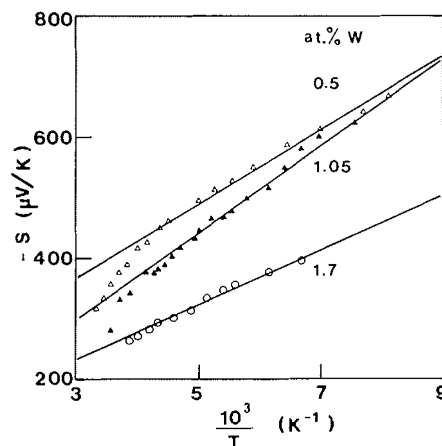

FIG. 3. The thermopower (S) of W-doped VO_2 plotted against $10^3/T$: △, 0.5 at.% W; ▲, 1.05 at.% W; ○, 1.7 at.% W; The values of $(E_{c0} - E_F)$ and A calculated from the straight lines shown are given in Table 1.

For an extrinsic semiconductor at high temperatures, an exhaustion region is expected with conductivity of the form

$$[2] \qquad \sigma = N_d(1 - \kappa)\mu e$$

where N_d is the donor concentration, κ is the compensation ratio (acceptor to donor ratio), μ is the conduction band mobility, and e is the electronic charge. At lower temperatures and for low compensations, a limited region may be observed with conductivity

$$[3] \qquad \sigma = (N_c N_d/2)^{1/2} \exp(-E_d/2kT)\mu e$$

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where N_c is defined as the effective density of states at the conduction band; $N_c = 4.83 \times 10^{15} (m^*/m)^{3/2} T^{3/2}$ cm^{-3}; E_d is the donor ionization energy; and m^*/m is the electron effective mass ratio. At still lower temperatures, the conductivity becomes

$$[4] \qquad \sigma = \tfrac{1}{2} N_c (1/\kappa - 1) \exp(-E_d/kT) \mu e$$

These expressions can be used to fit the conductivity data shown in Fig. 1 if a value for the mobility μ and its temperature dependence are known.

The most reliable estimates of μ are those of Rosevear and Paul (1973) and Kitahiro *et al.* (1966) made from Hall Effect measurements. The value obtained is $\mu = 0.5$ cm^2/Vs with a small temperature dependence. These measurements were made on undoped material and probably overestimate both the magnitude and the temperature variation of the mobility due to a contribution from hopping conductivity. Initially, therefore, we shall assume a constant mobility of 0.5 cm^2/Vs.

Using [4], plots of $\log_{10}(\sigma/T^{3/2})$ vs. T^{-1} at low temperatures yield values of E_d from 0.06 to 0.08 eV as shown in Table 1. A decreasing value of E_d with increasing donor concentration is consistent with similar phenomena in Ge and Si at high impurity concentrations where impurity band formation reduces E_d (Blakemore 1962; Ioffe 1960). The agreement between these values of E_d and the activation energies determined in the thermopower experiments provides justification for the assumption of a temperature dependent mobility.

In order to estimate the compensation ratio κ and the effective mass ratio, it is necessary to decide whether [2] or [3] is the most appropriate near the transition temperature T_t. It is known that the region corresponding to [3] may not be observed for very heavy compensation, and also that the condition for exhaustion is $E_d < 3kT$ (Blakemore 1962). The latter condition occurs at about 250 K for $E_d \sim 0.06$ eV, and this temperature range also corresponds to that where deviations occur from simple semiconductor behavior in the thermopower (Fig. 3). This suggests that near T_t, the conductivity is described by [2]. The procedure followed to obtain κ and m^* is illustrated for the sample with 1.05 at.% W, while results for all samples are given in Table 1.

From the data, the conductivities given by [2] and [4] are equal at about 250 K. Taking $E_d = 0.069$ eV we find the relation

$$[5] \qquad (m^*/m)^{3/2}/\kappa = 728$$

The intercept of $\log_{10}(\sigma/T^{3/2})$ vs. T^{-1} curve is 0.058 $(\Omega\ \text{cm})^{-1}/\text{K}^{3/2}$ and yields another relation

$$[6] \qquad ((1/\kappa) - 1)(m^*/m)^{3/2}\mu = 151 \text{ cm}^2/\text{Vs}$$

Taking $\mu = 0.5$ cm^2/Vs, these two relations give $m^* = 57\,m$ and the compensation ratio $\kappa = 0.59$.

The results are similar for other dopings, with $m^*/m = 67 \pm 10$ over the concentration range 0.67–1.70 at.% W. At lower impurity concentrations, smaller values of m^* and κ are obtained and this may reflect different conditions for the validity of [2]. The estimate of m^*/m agrees with that made by Zylbersztejn and Mott (1975) for niobium-doped VO_2 with impurity concentrations in the range 0.02 to 0.05 at.% Nb. It is also internally consistent since for the usual semiconductor theory to be applicable, the effective mass ratio has to be

$$[7] \qquad m^*/m > 2eh/3mkT\mu$$

(Frohlich and Sewell 1959). For $\mu = 0.5$ cm^2/Vs, m^*/m has to be greater than 60 at 300 K. It may be noted that $m^*/m \sim 60$ does not necessarily imply very narrow bands since the effective mass may be enhanced by polaron effects (Zylbersztejn and Mott 1975).

The large compensation ratios are consistent with the existence of impurity states within the energy gap of almost the same number as the W concentration (10^{19}–5×10^{20} cm^{-3}). Berglund and Guggenheim (1969) have estimated the impurity state concentration as 10^{20} cm^{-3} from optical data. The alternative assumption that [3] is valid near T_t gives rise to lower values of κ and m^* ($m^* = 16\,m$ and $\kappa = 0.1$ for the sample with 1.05 at.% W). However, this compensation ratio is still too large for [3] to be valid, and the values obtained can only be regarded as a lower limit of m^*.

The striking feature of W doping is the lowering of the transition temperature. It is known from NMR studies (Reyes 1974) and X-ray crystallography (Nygren and Israelsson 1969) that the low temperature semiconducting phase is the same as that for pure VO_2, and that no intermediate phases are formed at the transition. This contrasts with the effects of Cr (Marezio *et al.* 1972) or Al (Reyes *et al.* 1975). An interesting observation can be made for the relatively simple case of VO_2:W.

In a model proposed by Adler and Brooks

(1967), the metal–semiconductor transition is attributed to the effects of increasing crystalline distortion. The semiconducting energy gap, E_g is assumed to increase with the distortion and a one-dimensional calculation shows that E_g decreases with the free carrier concentration as

$$E_g = E_{g0} - \xi n$$

where E_{g0} is the energy gap at $T = 0$ and ξ is a function of the distortion. In the narrow band limit, the transition temperature is predicted as

$$E_{g0}/kT_t = 8.1$$

For an energy gap of 0.6 eV, this transition temperature is about 860 K which is much higher than the experimental value. Adler (1970) suggests that a three-dimensional treatment should make the results more reasonable.

The effects of impurities on the transition temperature can be predicted. For a donor concentration, x_d, in the exhaustion region, Adler *et al.* (1967) predict

$$E_{g0}/kT_t = 8.1(1 + 4x_d) + (x_d/2)\ln(1/x_d)$$

The presence of 1 at.% donor states results in a 4% reduction of the transition temperature. Without regard to absolute values, this is in good agreement with the results in VO_2:W.

5. Conclusions

The transport properties of tungsten-doped VO_2 can be interpreted in terms of n-type extrinsic conduction with donor states situated 0.06 to 0.08 eV below the conduction band. The extrinsic carriers can be used to probe the characteristics of the conduction band and an effective mass of $m^*/m = 65 \pm 10$ is obtained.

Acknowledgments

This work was supported by the Defence Research Board of Canada. Discussions with, and assistance from, Dr. A. Mansingh are gratefully acknowledged.

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