LETTER TO THE EDITOR

Note on the conduction mechanism of vanadium sesquioxide

1. *Introduction.* Earlier measurements performed on V_2O_3 by Foëx[1]) and Morin[2]) show a remarkable dependence of the resistivity, ρ, upon temperature the material being a good conductor ($\rho \sim 10^{-2} - 10^{-3}\,\Omega^1\,cm^1$) above 168°K, whereas at this temperature the conductivity drops to about $10^{-4}\,\Omega^{-1}\,cm^{-1}$, decreasing still further with temperature in an exponential way with an "activation energy" of about 0.20 eV. At 168°K a change in crystal structure has been found by X-ray diffraction experiments[3]). Morin supposes[2]) this jump in the conductivity to be due to a splitting of a partially filled band into two separate bands, the Fermi level being somewhere in between.

In the region between 220°K and 510°K an increase of resistivity by about a factor 2 with increasing temperature has been found, showing a small hysteresis (Foëx[1])). Above 510°K Foëx reports an increase of conductivity as $e^{-E_0/kT}$ with E_0 about 0.04 eV.

2. *Measurements.* It was the aim of the present investigation to add some experimental data, performing Hall and Seebeck measurements and if possible to deduce a model for the conduction mechanism.

All the measurements were made on sintered samples, prepared by reduction of NH_4VO_3 (ammonium metavanadate) and sintering at 1300°C or 1400°C under pure hydrogen.

The jump in conductivity at 168°K was used as a criterion for stoechiometry. Specimens with a conductivity ratio of at least 10^6 were used only.

Seebeck effect was measured from $-150°C$ up to 400°C. The thermopower, θ, was always found to be small ($+10\,\mu V/degree$) over the whole range above 168°K. Below 168°K the order of magnitude of θ was about $10^2\,\mu V/degree$, the precise values and the sign depending upon the composition. Below 168°K, judging from the Seebeck effect, n- or p-type V_2O_3, can be distinguished (see figure).

No Hall effect was found. The best estimates were:

$$R_H < 2 \times 10^{-3}\,cm^3\,coulomb^{-1} \text{ at } 300°K$$
$$R_H < 1,5 \times 10^2\,cm^3\,coulomb^{-1} \text{ at } 165°K,$$

so at the temperatures mentioned the Hall mobility was found to be smaller than 0.3 cm²/V sec and 0.05 cm²/V sec, respectively.

3. *Interpretation.* *a.* The temperature region between 168°K and 300°K. Here a remarkable small value for θ is found for all samples (figure 1). Interpreting this as the distance of the average conduction level, E, to the Fermi level E_F, by

$$E - E_F = e\theta T, \tag{1}$$

where e stands for the electron charge and T for the absolute temperature, it is found that

$$E - E_F < 3 \times 10^{-3} \text{ eV}.$$

This result suggests conduction by one type of carriers with the Fermi level lying within the band. The Hall coefficient R_H is found to be smaller than 2×10^{-3} cm^3 coulomb^{-1} at 300°K, so from

$$R_H \cong \frac{1}{ne} \qquad (2)$$

it should follow for the carrier concentration, n,

$$n > 3 \times 10^{21} \text{ cm}^{-3},$$

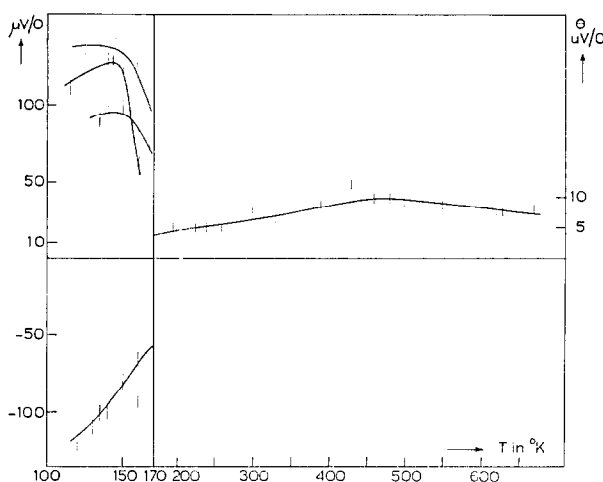also pointing to a metal type conduction.

Fig. 1. The thermo-power θ of V$_2$O$_3$ plotted as a function of absolute temperature.

b. The temperature region below 168°K. Below the transition temperature the activation energy, E_a, for the conductivity was found to be 0.2 eV while for all samples

$$|\theta| \sim 10^2 \text{ μV/degree,}$$

from which value the distance from conduction levels to Fermi level is found to be
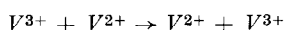
$$|E - E_F| \sim 10^{-2} \text{ eV.}$$

Such small distance cannot account for the large variation of conductivity with temperature found in the various samples. It seems likely, therefore, that the temperature dependence of the conductivity is not due to a variation of carrier concentration but to a variation of mobility, so
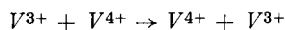
$$\mu = \mu_0 \, e^{-E_a/kT}. \qquad (3)$$

The low mobilities found, depending exponentially on temperature, suggest a jump type conduction process.

Since small deviations of stoechiometry occur, either donor or acceptor centres will be present; so even at low temperatures free electrons (or holes) are loosened from these centres at the cost of a small activation energy as was seen from the figure. These electrons, or holes, are supposed to be attached, then, to metal ions, the repeated reaction between neighbouring ions:

$$V^{3+} + V^{2+} \rightarrow V^{2+} + V^{3+}$$

or:

$$V^{3+} + V^{4+} \rightarrow V^{4+} + V^{3+}$$

representing the movements of the carriers. The activation energy for the mobility is essentially the same as the activation energy for the latter reactions. Also "intrinsic" conduction could be thought of, especially when very pure samples would have been studied, but in our cases at low temperatures the "extrinsic" process is probably dominating. In such a model a concentration of charge carriers of the order of

$$n \sim 10^{20} \text{ cm}^{-3}$$

would be reasonable. At 165°K this would lead to a mobility

$$\mu \sim 10^{-5} \text{ cm}^2/\text{V sec.}$$

Mobilities of this order at the temperature in question could be explained using the formula derived[4][5] for jump type conduction processes:

$$\mu = a \frac{ed^2\nu_0 \, e^{-E_a/kT}}{kT} \tag{4}$$

where d is the jump length ($\simeq 3 \times 10^{-8}$ cm), ν_0 an average phonon frequency and a entropy factor. In this case the activation energy E_a has to be taken as 0.2 eV.

From the Hall measurements at 165°K it was found for all samples

$$R_H \leq 10^3 \text{ cm}^3 \text{ coulomb}^{-1}$$

or

$$n \geq 10^{16} \text{ cm}^{-3}.$$

It is believed that the jump in conductivity at 168°K results from a change in mobility rather than from a change in carrier concentration.

c. The temperature region from 300°K up to 670°K' Above 510°K Foëx[1]) reports that the resistivity decreases with an exponential function exp E_a'/kT with $E_a' \simeq 0.04$ eV. In this region we found the thermo-power to be of the order of 10 μV/degree, so:

$$E - E_F \sim 5 \times 10^{-3} \text{ eV.}$$

This distance again seems too small to account for the exponential temperature dependence of σ, so in this region possibly again

$$\mu = \mu_0 \, e^{-E_a'/kT} \quad \text{with} \quad E_a' \simeq 0.04 \text{ eV.}$$

This would suggest a type of conduction somewhat alike that of case b, though with much smaller activation energy.

It has to be mentioned, however, that it appeared to be difficult to obtain the suitable reducing atmosphere in order to perform measurements at these higher temperatures without the material being deteriorated by changes in the chemical composition.

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LITERATURE

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