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# On the Mechanism of Electron Transport in Cr-Doped $V_2O_3$*

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Electrical conductivity, Seebeck coefficient, heat capacity, heat of transition, and high-temperature X-ray structure of $(Cr_xV_{1-x})_2O_3$ phases (with $x < 0.10$) have been studied. On the basis of these results, it is concluded that these phases are band conductors above the low-temperature transition. There is no firm evidence of a Mott-type transition.

## Introduction

The physical properties of Cr-doped $V_2O_3$ have been studied very extensively over the last five years (*1–6*). On the basis of this work it had generally been accepted (see especially Ref. (*5*)) that the electrical anomaly encountered in these alloys above room temperature is a manifestation of the Mott transition (*7*).

Our experimental investigation was motivated by the consideration that a mere rise in the electrical resistivity was not an adequate proof for a Mott transition. The characteristic features of this type of transition as originally proposed are: (1) a change from itinerant to localized electron conduction and (2) the discontinuous (first order) nature of this transition. A conclusive way to distinguish between the itinerant electron conduction and conduction by hopping via localized levels can only be obtained by combining the data on temperature dependence of electrical conductivity with the thermoelectric or Hall data. The other very meaningful experiment, which could throw considerable light on the transition mechanism would be the measurement of heat capacity as a function of temperature as also the heat and entropy of transition.

We have conducted several of these experiments and examined the tenability of the Mott-transition hypothesis in light of these new data (*8*). We review our recent experimental results and present evidence which throws considerable doubt on the validity of the earlier interpretation. We propose an alternative mechanism for the interpretation of the experimental results published so far.

## Experimental Work

Single crystals of $(Cr_xV_{1-x})_2O_3$ were grown by an arc-melting technique described by Fan and Reed (*9*); the total impurity content of the boules as determined by mass spectrometric techniques was of the order of 100 ppmw. Heat capacity measurements were carried out by means of a commercial scanning calorimeter; four-probe electrical resistivity and Seebeck coefficient measurements were carried out using automated bridge circuits with appropriate precautions to eliminate spurious voltages.

## Results and Discussion

The electrical resistivity ($\rho$) and Seebeck coefficient ($\alpha$) of $(Cr_xV_{1-x})_2O_3$ (with $x = 0$, 0.01, 0.014, 0.020, 0.033, 0.060, and 0.10) and $(Al_{0.0033}V_{0.9967})_2O_3$ have been measured as a

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function of temperature. For the purpose of presenting the results, we can classify these compositions in three groups: (i) $x < 0.01$, (ii) $0.01 \leqslant x < 0.02$, and (iii) $0.02 \leqslant x \leqslant 0.10$. The plots of log $\rho$ and $\alpha$ as a function of $1/T$ for three typical compositions (one from each group) are presented in Fig. 1. Special attention is drawn to the hump in the log $\rho - 1/T$ plot in the temperature region 300–600 K for compositions in group (ii), which has been attributed to a Mott-type transition. This region has been the main topic of our investigation in the present work. Our electrical resistivity data are quite consistent with the earlier reports (*1–5*). However, our Seebeck data shed new light on the mechanism. There is a close parallelism between the $\alpha(1/T)$ plots and the corresponding log $\rho(1/T)$ plots. The slopes are exactly equal for $x < 0.03$ in the temperature range of 220–650 K. This is generally taken to indicate that there is no activation energy associated with mobility. This seems to eliminate any transition to localized electron conduction. Furthermore, the Seebeck coefficient value after the anomaly is near +15 to +20 $\mu$V/°K. This small value would lead to an absurdly high value of $V^{4+}$ ion concentration on the "localized-electron" model, which would be inconsistent with the known stoichiometry of the sample.

Pettifer et al. (*10*) have studied the electrical resistivity and Hall coefficient as a function of temperature and composition on polycrystalline sintered samples of 1% Cr-doped $V_2O_3$. The Hall coefficient remained the same in sign and magnitude on both sides of the supposed Mott-transition. This is consistent with our finding that both the electrical resistivity and the thermoelectric values are nearly equal before and after the anomaly. Pettifer et al. (*10*) have similarly argued that

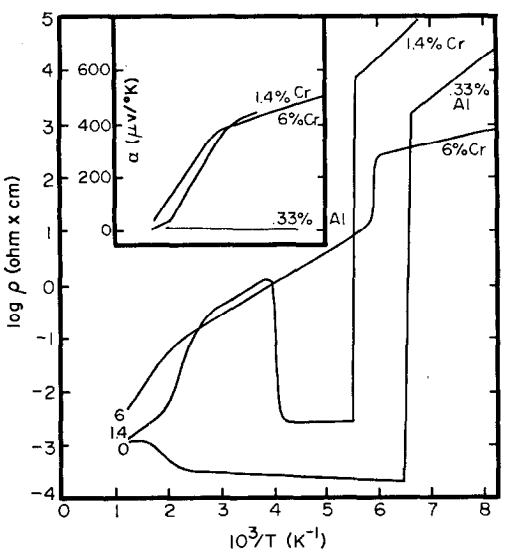


FIG. 1. Electrical resistivity (log$\rho$) and Seebeck coefficient ($\alpha$) as a function of reciprocal temperature for single crystals of $(Al_{0.0033}V_{0.9967})_2O_3$ (curve 1), $(Cr_{0.014}V_{0.986})_2O_3$ (curve 2), and $(Cr_{0.060}V_{0.940})_2O_3$ (curve 3). Abscissa scale on inset is in the range of $O = 10^3/T \leqslant 4$.

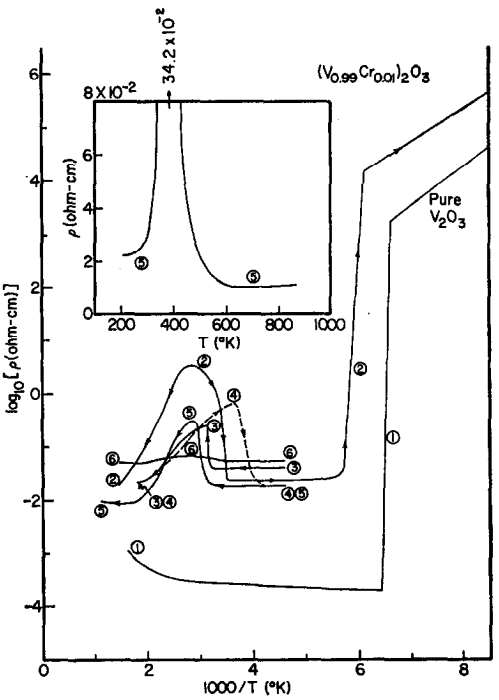


FIG. 2. Electrical resistivity (log$\rho$) as a function of reciprocal temperature for single crystals of $V_2O_3$ and $(Cr_{0.01}V_{0.99})_2O_3$. Curve 1, pure $V_2O_3$. Curve 2, virgin sample of $(Cr_{0.01}V_{0.99})_2O_3$ taken rapidly through the anomalous region. Slow heating (curve 3), fast cooling (curve 4), and finally slow heating again (curve 5) of another sample of $(Cr_{0.01}V_{0.099})_2O_3$. Insert curve 5 shown as $\rho$ vs $T$ plot to bring out the nearly temperature independent resistivity at high temperatures. Curve 6, a very tired sample of $(Cr_{0.01}V_{0.99})_2O_3$ through repeated heating and cooling.

it would be difficult to reconcile their experimental data with two different types of conduction mechanisms involved, i.e., band conduction before and conduction through localized states after the Mott transition.

A careful examination of our electrical resistivity results reveals that there is a change in the slope of $\log\rho(1/T)$ plots near 600 K. The slope beyond 600K (i.e., after the hump has been traversed) decreases considerably in all cases. For compositions with low $x(\sim 0.01)$, it is nearly zero. It was found that if the sample was heated slowly and allowed to stand at each temperature for a sufficient length of time, the width of the hump was considerably reduced and the flat portion in the high temperature resistivity plot became distinctly visible (Fig. 2). Such a temperature-independent resistivity is not at all consistent with any localized level transport. It was also found that the results in the anomalous region were highly sensitive to the thermal history of the sample. In samples which had been cycled repeatedly the hump nearly disappeared. At the same time no appreciable change was noticed in the low temperature transition, indicating that there was no change in the chemical composition.

High temperature powder X-ray diffraction studies of $(Cr_{0.01}V_{0.99})_2O_3$ in the temperature range of 300–700 K have shown that the room temperature rhombohedral phase (pseudo-hexagonal) undergoes a change in the region of anomaly to another isomorphous rhombohedral phase. Figure 3 shows the $30\bar{3}0$ (hexagonal index) diffraction line obtained at different temperatures from materials prepared under varying conditions. The gradual nature of the transition extending over a wide range of temperature and its dependence on the thermal history of the sample is clearly seen from Fig. 3.

A broad two-phase coexistence region coinciding with the region of electrical anomaly seems to be a common feature in all the $V_2O_3$ phases showing the high temperature anomaly (*11*). An X-ray examination of pure $V_2O_3$ in this temperature range has also revealed the presence of more than one phase coexisting from ~450 to at least 700 K (*12*). This is precisely the temperature region in which the electrical resistivity shows an anomalous rise. The multiphase coexistence in pure $V_2O_3$ in this temperature region has also been deduced by Kerlin et al. (*13*) on the basis of their NMR results. The reciprocal of the relaxation time $(1/T)$ rises with temperature and stays constant beyond 575 K. This fact is in line with our X-ray and electrical results; but contrary to the authors' assertion we do not see any evidence of a Mott-insulator

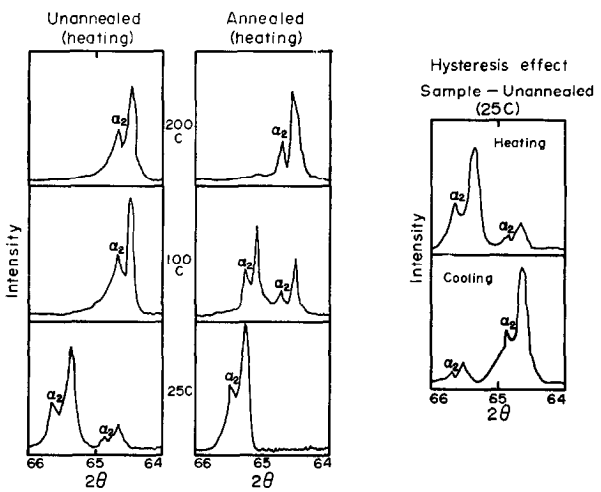


FIG. 3. X-ray powder diffraction line profile of the $30\bar{3}0$ reflection for $(Cr_{0.01}V_{0.99})_2O_3$ at different temperatures. Cu$K\alpha$ radiation ($\alpha_2$ peaks are marked, unmarked peaks are due to $\alpha_1$). The low angle pair is due to the high temperature phase and the one on the high angle side is due to the room temperature phase.

phase in these relaxation times. The relaxation time above 575 K is less than that for the room temperature metallic form, which is indicative of increased free electron density near the Fermi level. The relaxation time in an insulator should have been much higher.

Furthermore, in our measurements of the heat of transition we failed to detect any heat change at the anomaly within the experimental error of ±25 cal/mole. It is hard to reconcile this fact with a first order Mott transition. No doubt, the transition is gradual, extending over a wide range of temperature (as revealed by X-ray results which, by the way, is probably not due to any inhomogeneous distribution of Cr as suggested by several authors. The chromium distribution in our sample was monitored by SEM and microprobe technique and no inhomogeneity was detected over the area covered by the beam.) The gradual nature of the transition could to some extent decrease the intensity of the heat effect, but we do not expect it to be completely suppressed, if it was present, because at least 50% of the material transforms in a temperature interval of less than 50°.

In conclusion, our experimental results indicate that $V_2O_3$ and $(Cr_xV_{1-x})_2O_3$ (with $x < 0.10$) are band conductors in the entire temperature range and there is no firm evidence for any Mott-type of transition. The exact mechanism of the high temperature anomaly is not clear at this stage. However, it seems to be intimately connected with the coexistence of two phases, and possibly, to involve a complex intermediate state between the metallic regions.

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