Re-examination of the High-Temperature Resistivity Anomaly in $(Cr_{0.01}V_{0.99})_2O_3$†

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We report heat-capacity, x-ray, electrical-conductivity, and Seebeck-coefficient measurements in the range $200 < T < 900$ K, which indicate that there exist two high-temperature, band-type phases in $(Cr_{0.01}V_{0.99})_2O_3$. The electrical anomaly encountered in this range is considered to be an extrinsic phenomenon, attributed to the coexistence of these phases over a broad temperature range (~ 300–550 K). The data are inconsistent with any model invoking a metal-insulator transition in this range of temperature.

Recent work[1-6] on the electrical properties of $(Cr_{0.01}V_{0.99})_2O_3$ in the range $170 \leq T \leq 800$ K may be in need of reinterpretation in light of results shown in Fig. 1 for $(Cr_xV_{1-x})_2O_3$ with $0.008 \leq x \leq 0.012$. Our research was carried out on single-crystal specimens prepared by arc-melting techniques according to the method of Fan and Reed.[7] The total impurity content was in the range 100–150 ppm by weight, W (30 ppm by weight) and Ti (30 ppm by weight) being the principal contaminants. The Cr assay was obtained by electron microprobe analysis, and the impurity content was determined by mass spectrometry. These specimens appear to be superior to those grown by flux techniques[1-5] in which VN appeared as a separate phase. The material was exactly on stoichiometry: This was ascertained by reoxidation of samples to V_2O_5 and by the fact that single crystals could not be grown except by starting with needles of the exact stoichiometry; also, the low-temperature transition would not have been observed had the sample deviated significantly from the correct composition. Prolonged annealing at 1600°C under gettered Ar produced no detectable changes in composition.

The work presented here is consistent with the hypothesis that the high-temperature anomaly in electrical properties of $(Cr_{0.01}V_{0.99})_2O_3$ repre-

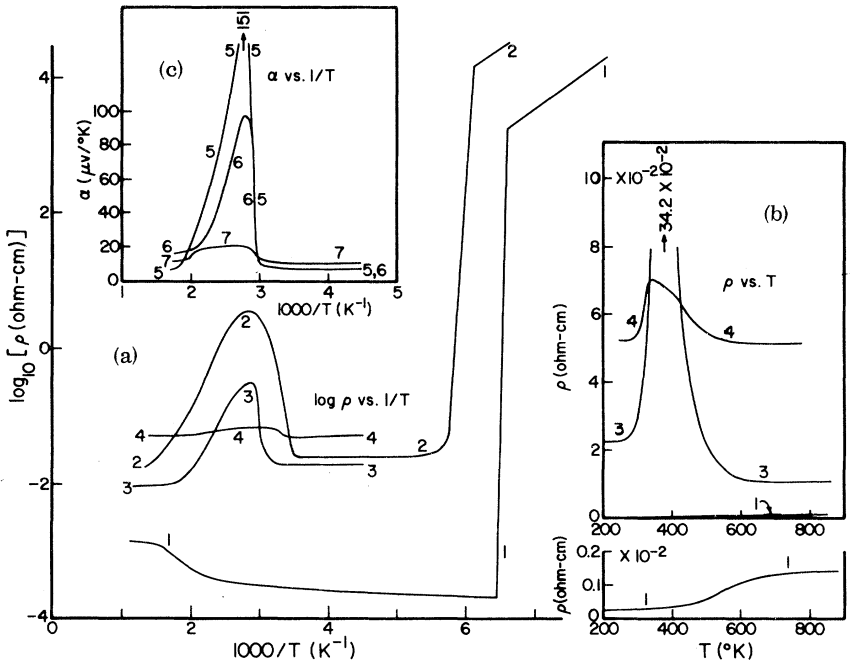

FIG. 1. Electrical properties of single-crystal V_2O_3 and $(Cr_{0.01}V_{0.99})_2O_3$. Curve 1: pure V_2O_3. Curves 2, 5: two virgin samples of $(Cr_{0.01}V_{0.99})_2O_3$ taken rapidly through the anomalous region. Curves 3, 6: same specimens taken slowly through the anomalous region. Curves 4, 7: specimens which had been cycled repeatedly through the anomalous region.

sents a two-phase, extrinsic phenomenon (such as a boundary scattering effect or trapping of carriers at internal grain boundaries formed during coexistence of two phases) rather than a metal-insulator transition as had previously been postulated. A number of experimental results in support of this hypothesis are cited below; the standard electrical measurements were carried out in a dynamic vacuum of 10^{-6} Torr, and a confirmatory run was performed in flowing gettered helium. The x-ray and heat-capacity measurements were taken under gettered and untreated helium, respectively.

(1) The high-temperature electrical anomaly reported earlier in the literature[1-6] was also encountered in the present experiment [curve 2, Fig. 1(a)], and in some samples was sufficiently sharp to simulate a first-order transition. However, every such discontinuity was characterized by the absence of any heat-capacity anomaly, and the corresponding enthalpy change in all cases was zero within the experimental error of ± 25 cal/mole.

(2) The size of the anomaly depended on the thermal history of the sample and on the rate of traverse of the temperature range $275 < T < 625$ K. By slow scanning (~ 2 deg/h) of this region the size of the anomaly could be greatly reduced [curve 3, Fig. 1(a)]. By heating or cooling samples that had repeatedly been cycled through the high-temperature range, the anomaly in this region could be almost totally suppressed [curve 4, Fig. 1(a)].

(3) On raising the temperature of samples that had exhibited a strong resistivity anomaly, one again observes metallic-type behavior [curve 3, Fig. 1(b), where ρ is plotted against T] above 600 K. (On rapidly cooling this specimen, the original anomaly reappeared at nearly full strength; this precludes the possibility of permanent changes such as appreciable conversion of surface layers to VO_2.) An incipient behavior of this type is in fact discernible in almost all previously published results, but the resistivity anomalies in earlier work extended over a much wider temperature range and thus masked the metalliclike behavior reported here. Rapid heating of our virgin samples also resulted in anomalies that extended over a much wider T range than indicated in Fig. 1. Thus, if a metal-insulator transition were to exist in $(Cr_{0.01}V_{0.99})_2O_3$ in the vicinity of 300 K, still a third, previously undetected insulator-metal transition would have to occur near 600 K to explain the observations above 600 K. The resistivity above 600 K generally fell below the resistivity observed in the range from 170 to 270 K. For comparison, our measurements on a single crystal of pure V_2O_3 are shown as curve 1, in Figs. 1(a) and 1(b). These agree with earlier studies[8,9] on single crystals of high quality.

(4) Precisely in the region of the electrical anomaly one encounters a two-phase domain as indicated by x-ray crystallography; on heating, the low-temperature rhombohedral phase (α phase) with $a_H = 4.957 \pm 0.005$ Å, $c_H = 13.99 \pm 0.01$ Å, $a_R = 5.471 \pm 0.005$ Å, $\alpha = 53°53' \pm 5'$ gradually gives way to the high-temperature rhombohedral phase (β phase) characterized by $a_H = 4.995 \pm 0.005$ Å, $c_H = 13.93 \pm 0.01$ Å, $a_R = 5.466 \pm 0.005$ Å, $\alpha = 54°22' \pm 5'$. The peak in the resistivity curve occurs at the temperature where the two phases are present in nearly equal amounts. The coexistence of two such phases in this temperature range had previously been recognized by other investigators.[3-7,10] Examination of specimens by the scanning electron microscope or by electron microprobe techniques revealed no inhomogeneities in Cr distribution within the limits of resolution of the instruments.

(5) Measurements of Seebeck coefficients, shown [curves 5–7, Fig. 1(c)] as plots of α versus $1/T$, show a close parallelism to the electrical measurements discussed in (2) and (3) above. The low values of α in the ranges 170–270 K and above 550 K, together with the known sample stoichiometries, appear to be consistent only with charge-carrier transport through bands in metallic, semimetallic, or band-type narrow-gap degenerate semiconductors.

In conclusion, the present data do not require invocation of a Mott-type transition to explain electrical anomalies encountered above 300 K. No meaningful interpretation can be provided for the electrical anomaly because it is encountered only in a two-phase coexistence region. The single β rhombohedral phase has a lower resistivity than the intermediate α rhombohedral phase. Both display positive temperature coefficients of resistivity as well as small and very weakly temperature-dependent Seebeck coefficients, which are irreconcilable with a hopping insulator that would have to be formed during a Mott transition.

Thus, while the gross features of the original phase diagram[3] are not disputed in the present publication, two important differences have emerged: (a) The phase boundary separating

α and β phases is extremely wide (see also Refs. 4, 10); (b) the β phase with $x = 0.01$, labeled as a Mott insulator in earlier publications, is either a metal, a semimetal, or a degenerate-band semiconductor. The occurrence of a critical point on the boundary between the two phases remains to be confirmed.

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Estimation of the Critical Temperature of Electron-Hole Droplets in Ge and Si

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The evaporation of electron-hole droplets is studied. Even at the critical temperature T_c, the electron-hole density of the fluid is large enough that it is not so badly represented by a plasma model. T_c is obtained using an expansion to the second order in T of the chemical potential $\mu(T, r_s)$ including correlation. The results of this crude method are in good agreement with experiments.

At $T = 0$ in an excited Ge-type semiconductor, a state of lower energy than the exciton exists and is an electron-hole plasma[1,2] with a density n_0 determined by minimizing the ground-state energy. As the electrons and holes are normally distributed throughout the sample at a density less than n_0, this plasma must concentrate into liquid droplets.

At $T = 4.2$°K the emission spectrum shows the coexistence of droplets and exciton peaks: The plasma droplets are dispersed in a gas. At $T = 15$°K, the droplet peak disappears and only gas remains. The purpose of this Letter is to study the nature of the gas below T_c and to estimate the critical temperature.[3] In the first part, we show that for very small T, the gas is composed essentially of excitons; this insulating phase transforms into a conducting gas of electrons and holes as T increases, so that near T_c the critical potential of the gas will be not so badly represented using the plasma model. In the second part, we calculate the critical temperature that appears graphically as an inflection point in the curve $\mu(T, n)$, where $\mu(T, n)$ is obtained as an expansion to the second order in T in which the calculation for $\mu(0, n)$ includes correlation effects. The results are in good agreement with experiments.

As T increases from zero, excited states become populated; they are all electron-hole configurations other than liquid, i.e., excitons, biexcitons, and electrons and holes (in a gaseous state). Equilibrium in the gas gives $2\mu_E = \mu_{BE} = 2(\mu_e + \mu_h)$, where μ_E, μ_{BE}, μ_e, and μ_h are the chemical potential of excitons, biexcitons, electrons, and holes, respectively. Liquid and gas equilibrium also require $\mu_E = \mu$, where μ is the