

High temperature resistivity characteristics of nonstoichiometric V_2O_3 *

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Abstract. The resistivity anomaly encountered in stoichiometric V_2O_3 is gradually suppressed with increasing density of cation vacancies. These observations are discussed in terms of related findings reported in the literature.

Keywords. Stoichiometric V_2O_3 ; resistivity; cation vacancies.

1. Introduction

It is by now well established that incorporation of excess oxygen into V_2O_3 generates cation vacancies, and that this process leads to serious disruptions in structure (Nakahira *et al* 1970; Novikov *et al* 1971; McWhan *et al* 1971; Nagasawa *et al* 1972; Ooshima 1973; Shirasaki and Ooshima 1973; Kuwamoto and Honig 1980; Ueda *et al* 1980), transport phenomena (Novikov *et al* 1971; McWhan *et al* 1971; Kozyreva *et al* 1972; Nagasawa *et al* 1972; Kimizuka *et al* 1973; Noguchi *et al* 1973; Launay *et al* 1976; Kuwamoto and Honig 1980; Ueda *et al* 1980), magnetic properties (Nakahira *et al* 1970; McWhan *et al* 1971; Zubkov *et al* 1972; Ooshima 1973; Ueda *et al* 1977, 1978, 1980), and optical characteristics (Novikov *et al* 1971; Kozyreva *et al* 1972). Prior work has concentrated on variations of electrical and magnetic characteristics and on changes in the metal-antiferromagnetic insulator transition of $V_{2(1-y)}O_3$ at low temperatures $T < 300$ K for $0 \leq y < 0.01$.

We report here briefly on alterations in electric properties in the range 300-900 K which arise from altering the oxygen/vanadium ratio in V_2O_3 ; this encompasses the region 400-600 K where stoichiometric V_2O_3 exhibits an anomalous rise in resistivity with temperature, first noted by Feinleib and Paul (1967), and subsequently verified by other investigators (Novikov *et al* 1971; McWhan *et al* 1971; Kozyreva *et al* 1972; Pettifer *et al* 1973; Honig *et al* 1974; Chandrashekar *et al* 1975; Kuwamoto *et al* 1980). These results will then be briefly discussed in the wider context of charge transport and metal-insulator transition mechanisms in V_2O_3 .

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2. Experimental

Single crystal specimens of appropriate size were cut from V_2O_3 boules that had been grown in a skull melter and were annealed in a variety of CO/CO_2 atmospheres to achieve different stoichiometries. The details of this procedure are discussed at length in preceding publications (Katsura and Hasegawa 1967; Wakihara and Katsura 1970; Shivashankar *et al* 1981).

Four probe resistivity measurements were then carried out in an automatic set up which provided for periodic reversal of the current direction so as to permit averaging out of spurious thermoelectric voltages. Silver paint was used for the attachment of leads. The results for three specimens are displayed in figure 1 as plots of resistivity ρ vs. temperature T . Also included is an earlier set of measurements (Chandrashekar *et al* 1975; Kuwamoto *et al* 1980) on V_2O_3 specimens grown in an arc melter (Fan and Reed 1972).

It is seen that the earlier results are in good accord with present measurements carried out on the most nearly stoichiometric material. Furthermore, with increasing departure from strict stoichiometry the size of the electric anomaly is reduced, and ultimately the anomaly is eliminated.

3. Discussion

The trend noted in figure 1 is similar to that encountered in the $(V_{1-x}Ti_x)_2O_3$ system with increasing Ti content (Chandrashekar *et al* 1975). Here, too, the

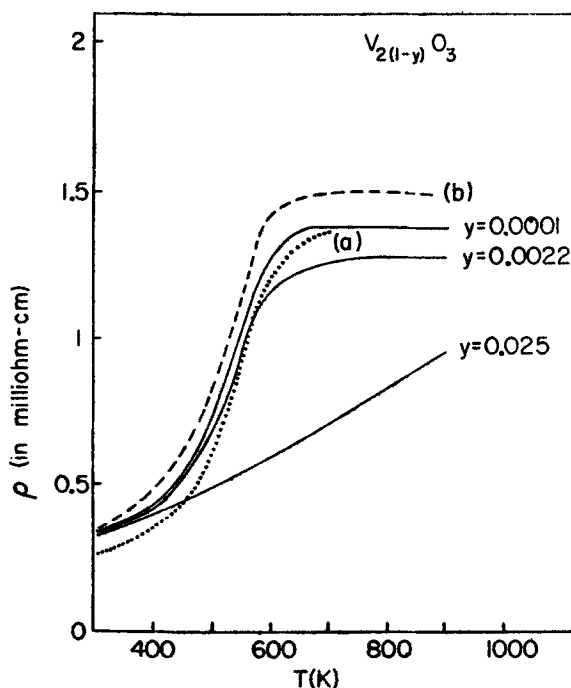


Figure 1. Resistivity (ρ) versus temperature (T) for $V_2(1-y)O_3$ single crystals ($0 \leq y \leq 0.025$). The results for as-grown single crystals of V_2O_3 are shown for comparison. Curve (a) (after Chandrashekar *et al* 1975); Curve (b) (after Kuwamoto *et al* 1980).

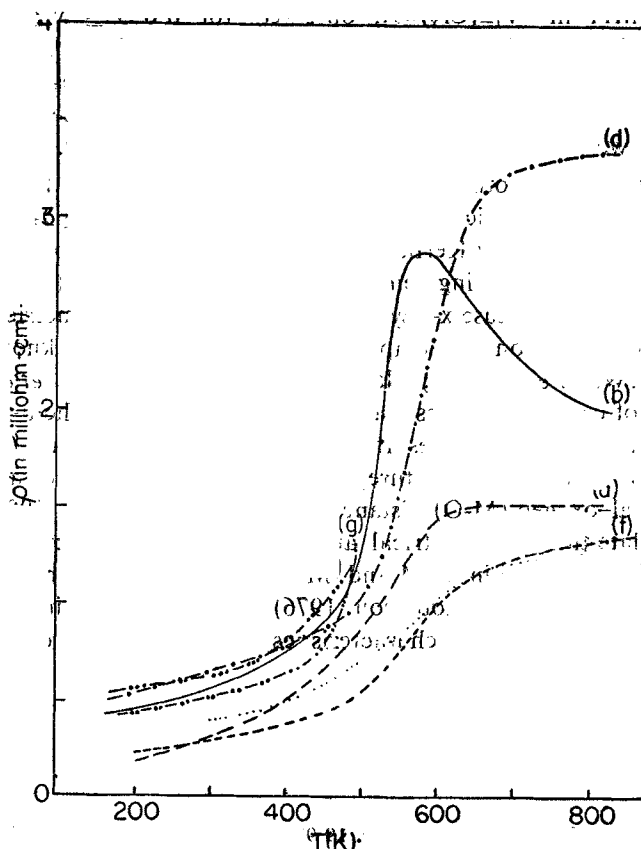


Figure 2. Resistivity (ρ) versus temperature (T) for single crystals of V_2O_5 . Curve (a) (after Kuwamoto *et al* 1980); Curve (b) (after McWhan *et al* 1971); Curve (c) (after Austin and Turner 1969); Curve (d) (after Feinleib and Paul 1967); Curve (e) (after Petitfer *et al* 1973); Curve (f) (after Hönig *et al* 1974); Curve (g) (after McWhan and Remeika 1970).

anomalous rise in resistivity is gradually suppressed with increasing x . The similarity in behaviour perhaps is not surprising since the introduction of excess oxygen or the substitution of Ti for V introduces two or one holes respectively into the band structure of the V_2O_5 host.

The present data also merit comparison with earlier work assembled in figure 2; only measurements extending well beyond 300 K are included.

Several discrepancies are apparent. The results by Feinleib and Paul (1967) indicate a larger anomalous rise in resistivity with temperature between 500 and 700 K than was observed by other workers. The measurements reported by the Bell Laboratories group (McWhan *et al* 1971) lead to an anomalous rise between 400 and 600 K, followed by an exponential drop of ρ with rising T beyond 600 K,

This latter feature has been interpreted by the authors as indicating that a continuous metal-insulator transition (MIT) takes place; this represents the extension of the sharp MIT in $(V_{1-x}Cr_x)_2O_3$, observed for $0.005 \leq x \leq 0.0018$, to the supercritical region. Such an interpretation is buttressed by nuclear magnetic relaxation measurements on V_2O_3 (Kerlin *et al* 1973). These were found to satisfy the Korringa relation below 550 K and to become independent of $T > 550$ K, as would be expected for a paramagnetic insulator.

However, since many other investigators have not observed features in the electrical properties that indicate the occurrence of a MIT in V_2O_3 , the claims by McWhan *et al* (1971) and by Kerlin *et al* (1973) should be accepted with caution. The electric anomaly with rising temperature cannot be directly correlated with variations in structure because x-ray diffraction on nonstoichiometric V_2O_3 has not been studied as a function of temperature. However, it is known (Nakahira *et al* 1970; McWhan *et al* 1971; Nagasawa *et al* 1972; Ueda *et al* 1980) that the generation of cation vacancies leads to a contraction of the *c*- and *a*- lattice parameters. This is also the result of increasing the pressure (McWhan and Remeika 1970) at room temperature, leading to a lessening of all metal-metal (M-M) and metal-oxygen (M-O) distances (Finger and Hazen 1980). One can therefore speculate that the electrical anomaly in stoichiometric V_2O_3 , being a concomitant of an increase in M-M and M-O distances with rising temperature (Robinson 1975; Rice and Robinson 1976), is suppressed in cation-deficient material because its structural characteristics approach those of metallic V_2O_3 under hydrostatic compression.

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