

Pressure effects on the semiconductor–semimetal transition in Ti_2O_3

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Abstract. Hydrostatic pressure has negligible effect on the resistivity anomaly and the c_H/a_H ratio of Ti_2O_3 . The results are consistent with the band-crossing mechanism wherein the a^T and e^T bands cross as the c_H/a_H ratio increases.

Keywords. Semiconductor-metal transition; pressure effects on Ti_2O_3 .

1. Introduction

There has been intense research activity in the last few years in the area of transition metal oxides exhibiting semiconductor-metal transitions (Goodenough 1971, Mott and Zinamon 1970, Rao and Subba Rao 1970, Hyland 1970). Among these oxides, V_2O_3 provides a situation where the transition (at 150°K) is first order and is associated with a change in crystal symmetry and a million-fold jump in conductivity; further, the antiferromagnetic ordering present in the low-temperature phase disappears above the transition temperature (Goodenough 1971, Mott and Zinamon 1970, Rao and Subba Rao 1970, Hyland 1970). The high-temperature metallic phase of V_2O_3 has a large c_H/a_H ratio (hexagonal basis) indicating a stabilization of the two bonding e^T orbitals per cation compared to the a^T band (Goodenough 1970, 1971). Ti_2O_3 , on the other hand, exhibits a higher-order transition (Hyland 1970, Rao *et al* 1968) around 413 K with a hundred-fold jump in conductivity (Honig and Reed 1968), but with no change in crystal symmetry (Rao *et al* 1968). It is paramagnetic both below and above the transition temperature (Moon *et al* 1969) and provides the simplest physical situation amongst oxides exhibiting semiconductor-metal transitions. The small c_H/a_H ratio of Ti_2O_3 in the low-temperature semiconducting phase indicates a positive trigonal field component and hence a filled, bonding a^T band below the empty e^T band (Goodenough 1970, 1971). The transition in Ti_2O_3 to the semi-metal phase is accompanied by an anomalous increase in the c_H/a_H ratio caused by an increase in the c_H parameter and a decrease in the a_H parameter (Rao *et al* 1968). Substitution of Ti^{3+} by V^{3+} in Ti_2O_3 enhances the c_H/a_H ratio (Loehman *et al* 1968) and a sample containing 10% V_2O_3 is metallic even at room temperature (Chandrasekhar *et al* 1970). Pressure has been used as an effective tool in probing the electronic transition in V_2O_3 (McWhan and Rice 1969, 1970). We have now investigated the effect of pressure on the electronic transition in Ti_2O_3 and some of its solid solutions with

V_2O_3 with a view to understanding the mechanism of the electronic transition, by carrying out resistivity and X-ray measurements.

2. Experimental

Single crystals of Ti_2O_3 and V-doped Ti_2O_3 were used for measurements. Samples of $1 \times 1.5 \times 10$ mm were etched and a metallic film was vacuum-deposited on the surface for good adherence of the bonding wires. Copper wires were bonded to the metal film, and tests were performed to ensure good ohmic contacts. Standard four-lead resistivity measurements were made using a constant dc current source. Continuous plots of resistance against temperature were made on an X-Y recorder (figure 1). High pressure measurements of resistivity were made in a piston-cylinder arrangement employing the teflon cell technique developed by Jayaraman *et al* (1967). Internal heating arrangement in the cell was employed for temperature variation, and a chromel-alumel thermocouple spotwelded in the close proximity of the sample enabled equilibrium measurements.

Lattice parameters were measured using a high pressure X-ray camera (Bassett 1967). Powder patterns were taken with samples enclosed between the anvil faces of small area. This enabled us to extend the measurements to very high pressures. Suitable calibration ensured hydrostatic pressure conditions between the anvil faces.

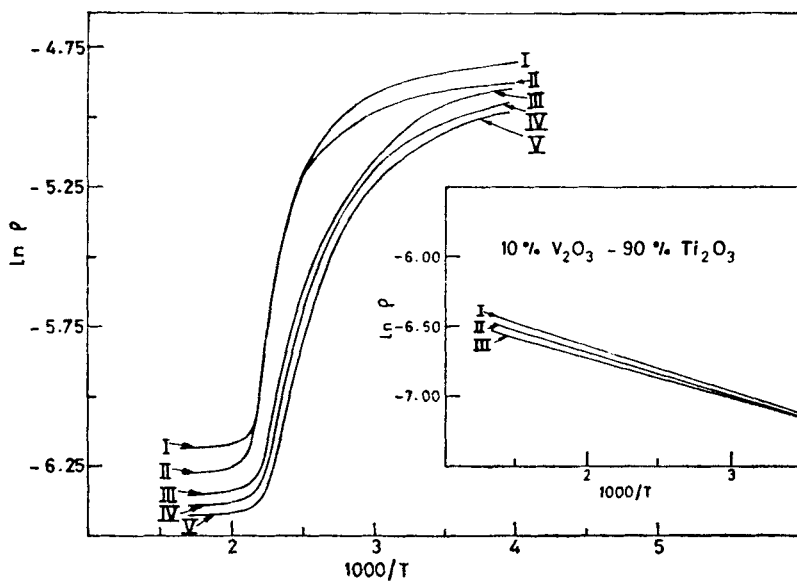


Figure 1. Plots of logarithm of resistivity (in ohm-cm) of Ti_2O_3 against reciprocal of absolute temperature. Curves I, II, III, IV and V are at 1 atm, 0.7 kbar, 3.7 kbar, 6.3 kbar, and 10.1 kbar respectively. In the insert plots of $\ln \rho$ against $1/T$ are shown for 10% V_2O_3 -90% Ti_2O_3 ; curves I, II and III are at 2, 6.3 and 10.4 kbar respectively.

3. Results and discussion

Figure 1 shows the plots of resistivity against temperature for pure Ti_2O_3 at a few

hydrostatic pressures. The resistivity anomaly at atmospheric pressure is of similar magnitude to that reported by Honig and Reed (1968) and Chandrasekhar *et al* (1970). Although the sample resistivity generally decreases with increase in pressure, the anomaly is essentially unaffected up to 10 kbar and dT_c/dP is very small. Resistivity measurements on 2.5% V-doped Ti_2O_3 at atmospheric pressure showed a smaller resistivity anomaly compared to pure Ti_2O_3 in agreement with the data of Chandrasekhar *et al* (1970). Here again, there was little or no change in the resistivity up to 20 kbar. Pressure data on 10% V-doped Ti_2O_3 (shown in the insert of figure 1) indicate that this sample remains metallic in the entire pressure-temperature range studied by us. The actual value of resistivity slightly decreases with increase in pressure just as in the case of pure Ti_2O_3 .

Hexagonal cell parameters, c_H and a_H , of Ti_2O_3 and 10% V-doped Ti_2O_3 are given at different pressures in table 1. It can be seen from the table that the c_H and a_H parameters of both these samples vary very little with pressure up to 100 kbar. The c_H/a_H ratio remains practically constant in the entire pressure range and the volume change is hardly 2% at 100 kbar. The resistivity data with pressure as well as the X-ray data are consistent with Goodenough's postulate (Goodenough, 1970) of the role of c_H/a_H ratio in the mechanism of the transition. These data allow an interpretation of the mechanism of the Ti_2O_3 transition as follows.

The crystal structure of Ti_2O_3 is corundum in both the semiconducting and semi-metal phases (Rao *et al* 1968). The cation-cation separation along the c -axis and in the basal plane are 2.59 Å and 2.99 Å respectively and are both below the critical separation of 3.02 Å only above which the 3d electrons are localised. Along the c -axis, cations exist in pairs and these pairs produce translational periodicity at a larger spacing (as shown by the magnitude of c in table 1). Such an aperiodic arrangement along the c -axis allows for a valence a^T band with a narrow band width, due to homopolar bonding of the cation pairs. At any finite temperature, thermal excitation of the carriers takes place across the gap (~ 0.02 eV) leaving holes in the a^T band. The hole, with a fairly large effective mass, attracts the surrounding anion octahedra towards it; this 'closing in' causes a local lattice deformation which alters the potential experienced by the electron at the valence site which enables it to escape the valence band. The extra kinetic energy available to the electron at the valence site renders the localisation of the electron energetically less probable, thereby leading to a reduction of the electron-hole excitation energy (reduction of the band gap). This process continues and a feedback essential for the phase transition is developed. Such a process continuously stabilises the e^T band at the cost of a^T band, causing the continued lattice distortion (rise in c/a ratio) observed in Ti_2O_3 (Goodenough 1970, Rao *et al* 1968). The feedback process discussed above explains the anomalous conductivity observed in the interval 400-500 K.

Table 1. X-ray data on Ti_2O_3 and 10% V_2O_3 -90% Ti_2O_3 at different pressures

Pressure	c_H Å	a_H Å	c_H/a_H	c_H Å	a_H Å	c_H/a_H
		Ti_2O_3		10% V_2O_3 -90% Ti_2O_3		
1 atm	13.811	5.181	2.666	13.894	5.132	2.707
60 kbar	13.717	5.143	2.667	13.849	5.112	2.710
100 kbar	13.720	5.117	2.681	13.783	5.072	2.717

Application of hydrostatic pressure on the sample tends to squeeze ions in all directions and the compression due to pressure is opposed and compensated by the aforementioned changes in c and a directions. This could lead to a vanishingly small net change in the cell parameters with respect to pressure and hence the low compressibility (table 1)*. The variation of unit cell volume with temperature (Rao *et al* 1968) as compared to the low compressibility ($\sim 2\%$ over 100 kbar) as well as the negligible effect of pressure on the resistivity anomaly is appreciable in terms of the mechanism initiated by the hole-lattice interaction in Ti_2O_3 . The volume effects with respect to temperature and pressure can be rationalised in terms of Ehrenfest's relation for higher order transitions (Rao and Rao 1967) to explain the small dT_c/dp ($\sim 0.5^\circ\text{C/kbar}$). It is interesting that we observe the same behaviour in c/a ratio with pressure in the sample $90\% Ti_2O_3 + 10\% V_2O_3$ which is a semi-metal with a negative gap (e^T band stabilised below the a^T band). These features of the Ti_2O_3 transition seem to be consistent with a band-crossing mechanism, rather than band overlap, (Goodenough 1971, Van Zandt *et al* 1968), with increasing temperature or increasing c_H/a_H ratio.

Recently, Kumar and Sinha (1971) have worked out a preliminary theory for semiconductor-metal transitions with an excitation-dependent gap and a consequent volume change accompanying the transition which seems to agree with experimental data. Zeiger, Kaplan and Raccach (1971) have presented a free-energy description of a smooth semiconductor-semimetal transition based on a two-band model which includes electron-electron Coulomb energy and lattice displacement energy. It is interesting that Mooradian and Raccach (1971) observe the softening of the A_{1g} phonon mode of Ti_2O_3 due to the extension of the Ti-Ti bond length along the c -axis in the same temperature interval as the variation of the c_H/a_H ratio variation (or the resistivity anomaly). From a macroscopic view point, the entropy change due to band-crossing and phonon softening may still be viewed as the 'thermodynamic' driving force for the transition in Ti_2O_3 .

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*Uniaxial stress measurements on Ti_2O_3 would be worthwhile.

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