

Metal-insulator transitions in Cr-doped V_2O_3 by x-ray and ultraviolet photoelectron spectroscopy*

M S HEGDE and S VASUDEVAN

Solid State and Structural Chemistry Unit, Indian Institute of Science,
Bangalore 560 012

MS received 15 June 1978; revised 28 August 1978

Abstract. X-ray and ultraviolet photoelectron spectroscopy have been employed to investigate the high temperature metal-insulator transitions in V_2O_3 and $(V_{0.99}Cr_{0.01})_2O_3$. The high temperature transitions are associated with more gradual changes in the 3d bands compared to the low-temperature transitions.

Keywords. Metal-insulator transition; Mott transition; ESCA; photoelectron spectroscopy.

1. Introduction

The metal-insulator transition of V_2O_3 around 170K accompanied by a phenomenal, ten million-fold jump in electrical resistivity has been investigated in detail (Mott 1974; Rao and Subba Rao 1974). V_2O_3 also exhibits an anomalous increase in resistivity above 300K as shown in figure 1. The resistivity of V_2O_3 at room temperature is considerably larger than that of 'real' metals like copper suggesting thereby that this oxide may be at the edge of a crystal configuration which can hardly sustain collective electrons in very narrow bands. One would, therefore, expect that by further dilation of the lattice, an insulating state would be attained wherein electron correlations would play a dominant role (as in Mott-Hubbard insulators). McWhan *et al* 1969 and McWhan and Remeika (1970) at the Bell Telephone Laboratories using Cr_2O_3 as dopant to dilate the V_2O_3 lattice, indeed observed a second metal-insulator transition above 325K. With about 1 at% of Cr, the resistivity increases by about 2 orders of magnitude in the 325-550K range and again drops with a further increase in temperature as shown in figure 1 (after Kuwamoto *et al* 1976). This transition is not accompanied by a change in crystal symmetry unlike the 170K transition (McWhan *et al* 1969; Pettifer *et al* 1973). The unit cell volume of the semi-conducting phase (above 500 K) is, however, larger than that of the metallic phase. On the basis of this as well as other factors, McWhan and Remeika (1970) and McWhan *et al* (1973) proposed that the high temperature transition in Cr-doped V_2O_3 was a manifestation of the Mott transition. This model has been questioned by a few workers (Zeiger 1975; Honig *et al* 1974; Kuwamoto *et al* 1976). We have studied the x-ray and ultraviolet photoelectron spectra of 1 at% Cr-doped V_2O_3 at different temperatures to throw light on the mechanism of the high-temperature metal-insulator transitions

*Communication No. 20 from Solid State & Structural Chemistry Unit.

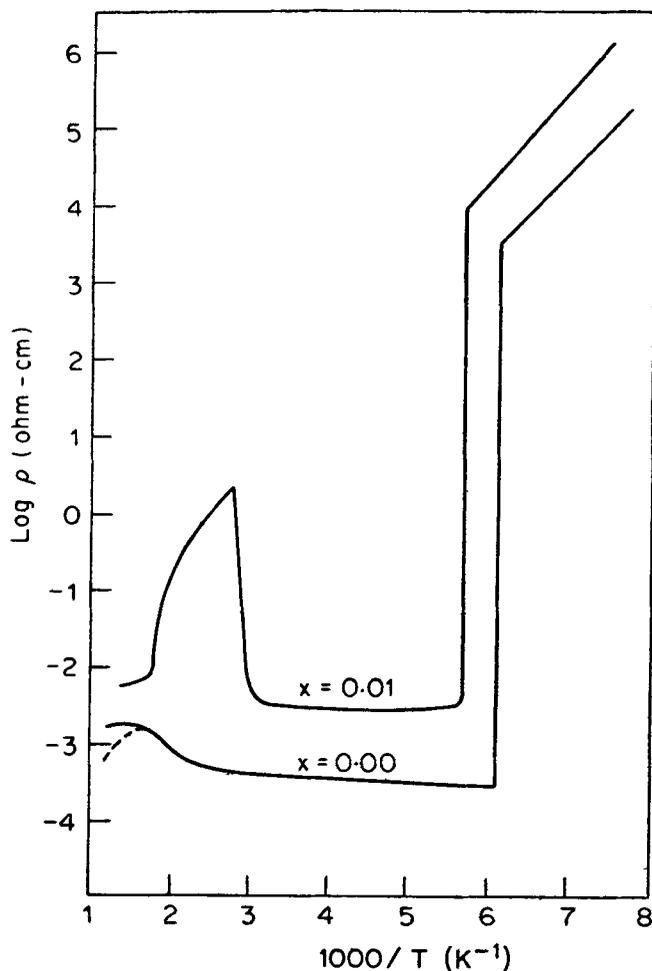


Figure 1. Electrical resistivity versus reciprocal temperature for $(V_{1-x}Cr_x)_2O_3$; $x=0.00$ and 0.01 . The dotted curve in the high temperature region of V_2O_5 is that found by McWhan *et al* (1971, 1975) while the full line represents the data of Kuwamoto *et al* (1976).

in this material. It has been shown recently that photoelectron spectroscopy provides a useful tool to examine changes in the electronic structure of metal oxides accompanying metal-insulator transitions (Vasudevan *et al* 1978).

2. Experimental

Crystals of pure V_2O_5 and $(V_{0.99}Cr_{0.01})_2O_5$ were grown by the arc method at Purdue University. X-ray and ultraviolet photoelectron spectra were recorded using an ESCA-3 Mark II spectrometer of VG Scientific Limited UK, fitted with a sample preparation chamber. The operating vacuum was 10^{-10} torr. The sample preparation chamber was fitted with an argon ion gun and a quadrupole mass spectrometer. The radiations employed were Al K $_{\alpha}$ (1486.6 eV), HeII (40.8 eV) and HeI (21.21 eV).

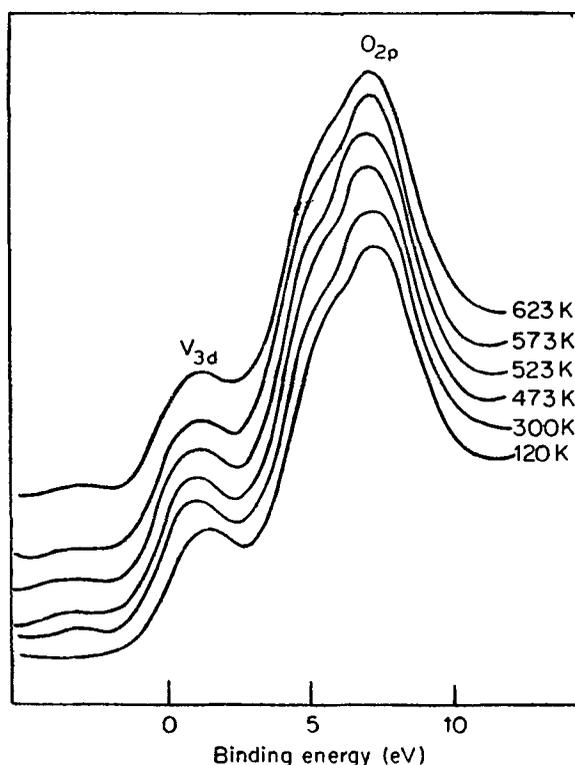


Figure 2. Valence band in the XPES of pure V_2O_3 at different temperatures.

The surfaces of the samples were cleaned under vacuum until reproducible spectra (particularly $O(1s)$ bands) were obtained. The uncertainty in band positions in the d band region is 0.1 eV.

3. Results and discussion

X-ray photoelectron spectra (XPES) of V_2O_3 at different temperatures are shown in figure 2. The spectra of all such oxides generally show the $3d$ band distinctly. The $O(2p)$ bands appearing at higher energies have a shoulder on the lower energy side and these bands are ascribed to metal-oxygen bonding. A comparison of the XPES at 120K and 300K shows that the $3d$ band shifts sharply by 0.5 eV towards lower binding energies in the room temperature metallic phase, a behaviour also found in other oxides undergoing metal-insulator transitions (Vasudevan *et al* 1978). Correspondingly, a modest band gap should be present in the low temperature insulating state. The $3d$ band shifts to slightly higher binding energies (by 0.25 eV with respect to the band at 300K) when V_2O_3 is heated to higher temperatures (see the spectrum at 573K in figure 2), but this shift appears to be gradual. This is consistent with the anomalous increase in resistivity between 300 and 550K referred to earlier. At still higher temperature the band again shifts to lower binding energies and the band position is close to that of the room temperature metallic phase. This is in

accordance with the observation of the Bell group (McWhan *et al* 1971, 1975) that the resistivity decline exponentially above 550K. It is also to be noted that the d band intensity does not show any significant changes through the high temperature transition.

Another feature in the XPES of V_2O_3 in figure 2 is noteworthy. The room temperature metallic phase shows a peak at a binding energy lower than that of the $3d$ band which may be due to a plasmon band (Hedin 1964). This band appears to be prominent when the resistivity of V_2O_3 is lowest (see curves at 300K and 623K). In figure 3 we have shown the XPES of $(V_{0.99}Cr_{0.01})_2O_3$ at several temperatures. The low temperature metal-insulator transition in this material is seen in terms of a sharp shift of the $3d$ band just as in pure V_2O_3 , the band being at lower energies (by 0.7 eV) in the room temperature metallic phase. The $3d$ band gradually shifts to slightly higher binding energies by 0.3 eV at higher temperatures (see the 423K curve figure 3) where there is a second metal-insulator transition. At still higher temperatures, however, when the material gradually comes back to the 'metallic' state, the $3d$ band shifts again to lower energies by 0.2 eV with respect to the band at 573K (see the 673K curve in figure 3). It is interesting that the $3d$ bands around room temperature and above 600K are almost identical. This is in accord with the fact that the resistivity of $(V_{0.99}Cr_{0.01})_2O_3$ above 600K is not far from the value encountered in the 180-325K range where the alloy is surely metallic. The d band intensity does not

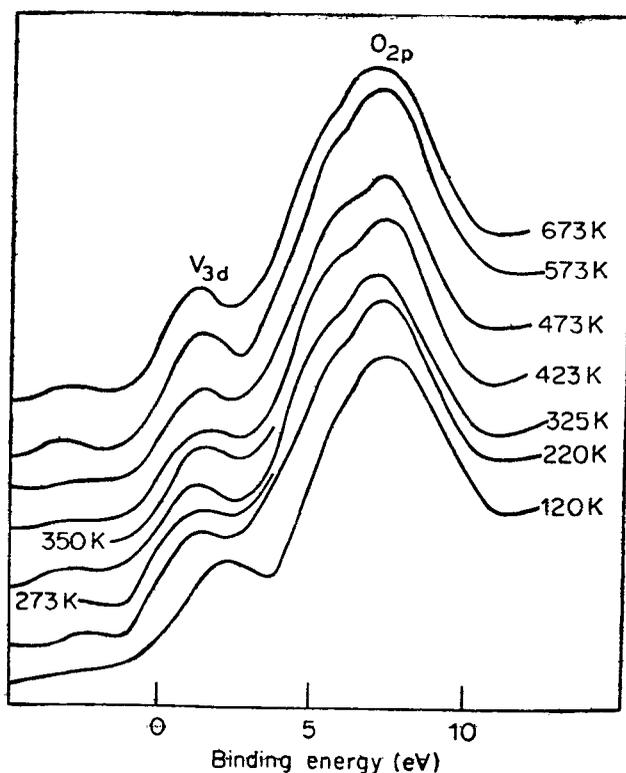


Figure 3. Valence band in the XPES of $(V_{0.99}Cr_{0.01})_2O_3$ at different temperatures.

show any significant changes in the 325–600K range. The plasmon band at low binding energies is prominent only in the ‘metallic regime’ (in the temperature ranges 180–325K and 570–680K).

The important core levels of V_2O_3 and $(V_{0.99}Cr_{0.01})_2O_3$ at different temperatures are listed in table 1. With the exception of the 3s level, the other levels of V_2O_3 do not change through the metal-insulator transitions. The 3s level shifts to lower binding energies (by 0.4 eV) at the 150K metal-insulator transition of V_2O_3 . The shift in the corresponding transition of the Cr-doped sample is negligible. This may be because the Cr-doped sample is a poorer metal than pure V_2O_3 at ordinary temperatures. There is no change in core levels through the high-temperature transitions of both the pure and Cr-doped samples.

In order to ensure that the XPES truly reflect changes in the valence band of $(V_{0.99}Cr_{0.01})_2O_3$, we recorded the ultraviolet photoelectron spectra (UVPES) of this alloy at different temperatures employing both HeII and HeI radiations. The results are shown in figure 4. The UVPES curves clearly show the expected 3d band shifts at the low temperature metal-insulator transition. The HeII spectrum at 550K corresponds to the insulator state of the high temperature metal-insulator transition. At this temperature, the 3d band is at a slightly higher energy (by 0.3 eV) than in the room temperature metallic phase. At still higher temperatures, however, the 3d band becomes identical to that of the room temperature metallic phase as clearly shown by the HeI spectra at 300K and 600K (see the inset of figure 4.).

Based on XPES and UVPES studies we conclude that the insulating state associated with the second metal-insulator transition of $(V_{0.99}Cr_{0.01})_2O_3$ in the 325–550K range has no unusual features (appreciably different from those of pure V_2O_3 in this range). The shift of the 3d band in the 325–550K range is in fact, smaller than that found in the case of the low temperature metal-insulator transition. It is generally believed that a Mott insulator is characterised by a localised electron configuration. While it is difficult to employ electrical resistivity or thermopower to determine whether a Mott insulating state is present or not (Mott 1967; Mott and Zinamon 1970), it is hard to think of a highly conducting Mott state which renders the PES or the resistivities around 300 and 600K to be nearly identical. The explanation of the high temperature metal-insulator transition in $(V_{0.99}Cr_{0.01})_2O_3$ could therefore be based

Table 1. Core level binding energies* in eV.

| | V_2O_3 | | | 1% Cr. V_2O_3 | | |
|-------|----------|------|----------------|-----------------|------|----------------|
| | 3p | 3s | 2p | 3p | 3s | 2p |
| 120 K | 39.9 | 68.3 | 515.5 523.0 | 40.1 | 68.6 | 515.2 522.7 |
| 300 K | 39.6 | 67.9 | 515.2 522.5 | 40.1 | 68.5 | 515.2 522.7 |
| 600 K | 39.5 | 67.9 | 515.2 522.5 | 40.1 | 68.5 | 515.2 522.7 |

*With reference to the Fermi level of Au.

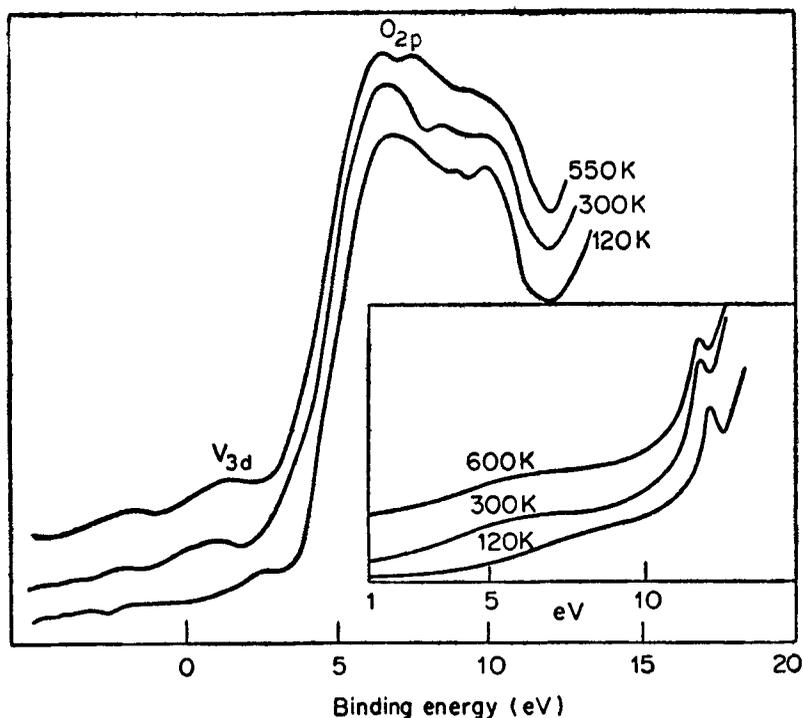


Figure 4. Valence band in HeII PES of $(V_{0.99}Cr_{0.01})_2O_3$ at different temperatures; in the inset, He I spectra are shown.

on some other considerations. One possibility is to attribute the transition to the presence of charge density waves (Kuwamoto *et al* 1976); another is to interpret the transition in terms of the shift in the degree of band overlap arising from changes in V-V and V-O distance (Zeiger 1975). The photoelectron spectra recorded by us, however, do not show any definite features (Pollak and Hughes 1976) ascribable to the presence of charge density waves. The gradual shift of the d band in the high temperature transition is somewhat similar to the temperature variation of the carrier concentration or normalised lattice parameter described by Zeiger for the transition of Ti_2O_3 or of V_2O_3 (at high temperatures).

Acknowledgements

The authors are thankful to the Department of Science and Technology, Government of India, for support of this research. Their thanks are due to Professor J M Honig of Purdue University for the oxide samples and for his helpful comments and to Professor C N R Rao for guidance and suggestions.

References

- Hedia L 1964 in *X-ray spectroscopy* ed. L V Azaroff (New York: McGraw-Hill)
 Honig J M, Chandrasekhar G V and Sinha A P B 1974 *Phys. Rev. Lett.* **32** 13

- Kuwamoto H, Keer H V, Keem J E, Shivashankar S A, Van Zandt L L and Honig J M 1976 *J. Phys.* **C4** 35
- McWhan D B, Rice T M and Remeika J P 1969 *Phys. Rev. Lett.* **23** 1384
- McWhan D B and Remeika J P 1970 *Phys. Rev. Lett.* **B2** 3734
- McWhan D B, Menth A and Remeika J P 1971 *J. Phys.* **C1** 1079
- McWhan D B, Menth A, Remeika J P, Brinkman W F and Rice T M 1973 *Phys. Rev.* **B7** 1920
- McWhan D B, Jayaraman A, Remeika J P and Rice T M 1975 *Phys. Rev. Lett.* **34** 547
- Mott N F 1967 *Adv. Phys.* **16** 49
- Mott N F 1974 *Metal-insulator transitions* (London: Taylor-Francis)
- Mott N F and Zinamon Z 1970 *Rep. Prog. Phys.* **33** 881
- Pettifer R F, Pitt G D, Thomas D and Vyas M K R 1973 *Mat. Res. Bull.* **8** 87
- Pollak R A and Hughes H P 1976 *J. Phys.* **C4** 151
- Rao C N R and Subba Rao G V 1974 *Transition metal oxides NSRDS monograph 49* (Washington : National Bureau of Standards)
- Vasudevan S, Hegde M S and Rao C N R 1978 *Solid State Commun.* **27** 131
- Zeiger H J 1975 *Phys. Rev.* **B11** 5132