

## Charge-transfer satellites in the x-ray photoelectron spectra of $3d^0$ and $4d^0$ metal oxides\*

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**Abstract.** O ( $2p$ )-metal ( $d$ ) charge-transfer satellites in core level spectra of  $3d^0$  metal ions in CaO,  $Sc_2O_3$ ,  $TiO_2$  and  $V_2O_5$  and  $4d^0$  ions in SrO,  $Y_2O_3$ ,  $ZrO_2$  and  $Nb_2O_5$  have been reported. A systematic increase in the satellite separation is noticed going from CaO to  $V_2O_5$  and from SrO to  $Nb_2O_5$ .

**Keywords.** Photoelectron spectra ; satellites.

### 1. Introduction

When a core electron from an insulating compound is ionised, smaller peaks called satellites are observed towards the higher binding energy of these primary peaks in the x-ray photoelectron spectra. Thus, oxides of  $3d$  transition metals like NiO, CoO, CuO exhibit such satellites (Rao *et al* 1979). A comprehensive study of satellites in transition metal compounds has been carried out by Vernon *et al* (1976). Charge-transfer from ligand to metal as proposed by Wallbank *et al* (1973) and Kim (1974) has been recognised as the most likely explanation for such satellites.

Core level spectra of  $3d^0$  transition metal ions in  $Sc_2O_3$ ,  $ScF_3$ ,  $TiF_4$  and  $TiO_2$  show satellites in the 10–15 eV range (Vernon *et al* 1975; Kim and Winograd 1975; Frost *et al* 1976). The origin of the satellites in  $Sc_2O_3$  and  $TiO_2$  has been assigned due to O ( $2p$ )-metal ( $3d$ ) charge transfer. We have recorded x-ray photoelectron spectra of a series of  $3d^0$  (CaO,  $Sc_2O_3$ ,  $TiO_2$  and  $V_2O_5$ ) and  $4d^0$  (SrO,  $Y_2O_3$ ,  $ZrO_2$  and  $Nb_2O_5$ ) metal oxides to investigate the satellites. We find a systematic increase in the satellite separation with increasing oxidation state of the metal ion or charge on the metal ion.

### 2. Experimental

Analytical grade commercial samples of metal oxides are used in this study. X-ray photoelectron spectra of  $3d^0$  and  $4d^0$  oxides are recorded in ESCA

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3-Mark II spectrometer of V.G. Scientific Limited, England. Since some of the oxides get reduced by  $\text{Ar}^+$  ion bombardment, no ion beam etching of the samples was carried out. There were no observable differences in the binding energies of core levels and also the satellite positions when the oxides were kept in the UHV chamber for more than 24 hr.

### 3. Results and discussion

In figure 1,  $2p_{3/2}$ ,  $2p_{1/2}$  bands of metal ions in  $\text{CaO}$ ,  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$  and  $\text{NH}_4\text{VO}_3$  are shown along with the satellites. The  $3d$  bands of metal ions in  $\text{SrO}$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{ZrO}_2$  and  $\text{Nb}_2\text{O}_5$  are shown in figure 2. Positions of the satellites in all the oxides studied are listed in table 1. In the case of  $\text{V}_2\text{O}_5$ , we have assigned the shoulder on the higher binding energy side of  $\text{O}(1s)$  peak to the satellite of the  $\text{V}(2p_{3/2})$  band; this satellite had not been noticed by earlier workers (Jorgenson 1976). The present assignment is justified by the presence of a similar shoulder in  $\text{NH}_4\text{VO}_3$ . That the shoulder is not due to some other oxygen species is established by the fact that such a shoulder is not found in the  $\text{O}(1s)$  bands of  $\text{VO}$ ,  $\text{V}_2\text{O}_3$  and  $\text{VO}_2$ . Also, the satellite corresponding to  $\text{V}(2p_{1/2})$  is also clear from the figure.

A detailed XPS study of  $\text{TiO}_2$  by Scrocco (1979) and of  $\text{TiO}_2$  and  $\text{BaTiO}_3$  by Chermette *et al* (1980) has shown that the  $13.5\text{ eV}$  satellite in  $\text{Ti}^{4+}$  is due to  $3e_g \rightarrow 4e_g$

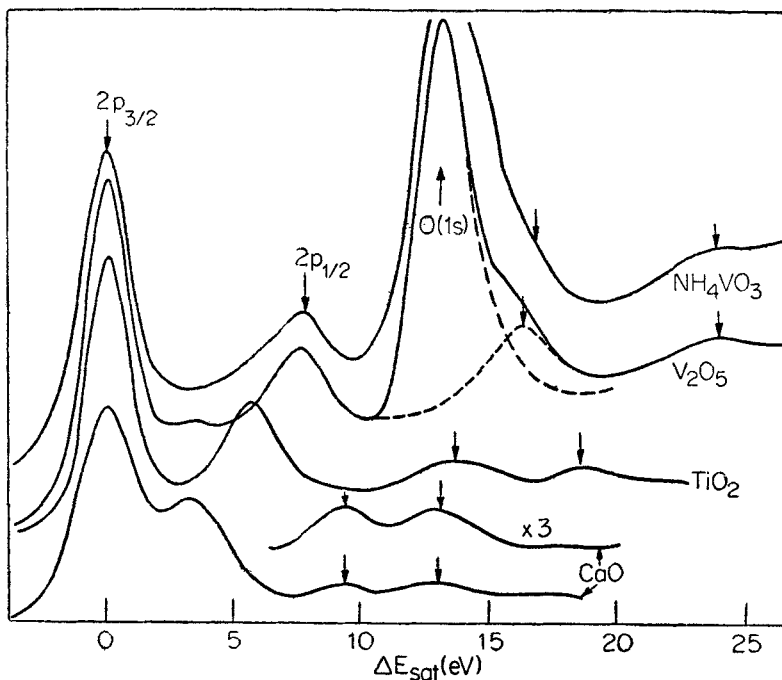


Figure 1. Metal  $2p$  bands in the XPS of  $\text{CaO}$ ,  $\text{TiO}_2$ ,  $\text{V}_2\text{O}_5$  and  $\text{NH}_4\text{VO}_3$ . The relative positions of the abscissa is adjusted so that the  $2p_{3/2}$  peak positions coincide. Satellite positions are marked by arrows.

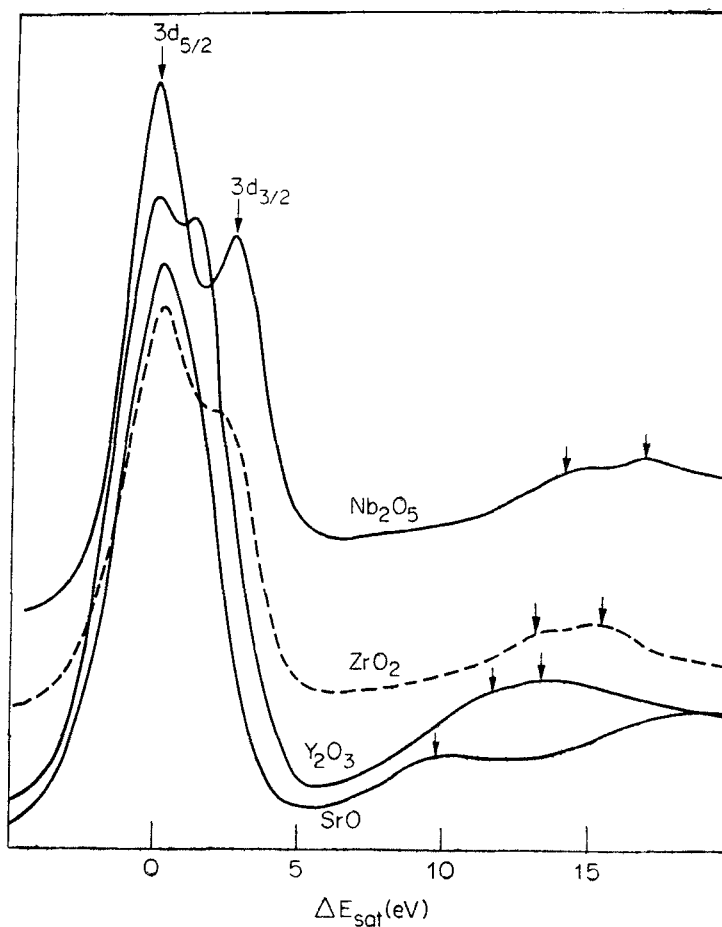


Figure 2. Metal 3d bands in the XPS of SrO, Y<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub>. 3d<sub>3/2</sub> is adjusted to zero.

Table 1. Energy separation of the satellite from the primary peak in eV.

Oxide	3p	3s	2p <sub>3/2</sub>	2p <sub>1/2</sub>	2s
CaO	9.5	..	9.1	9.1	..
Sc <sub>2</sub> O <sub>3</sub>	12.4	12.0	11.3	11.3	12.0
TiO <sub>2</sub>	13.4	13.1	13.5	13.4	13.4
V <sub>2</sub> O <sub>5</sub>	15.5	15.5	15.8	15.9	..
	3d		3p <sub>3/2</sub>	3p <sub>1/2</sub>	
SrO	10.5		10.0	10.0	
Y <sub>2</sub> O <sub>3</sub>	12.7		12.5	12.5	
ZrO <sub>2</sub>	13.3		13.2	13.0	
Nb <sub>2</sub> O <sub>5</sub>	15.3		15.8	15.8	

**Table 2.** Energy separation of satellites from the main peaks in some metal oxides and halides.

Compound	$\Delta E_{sat}(2p_{3/2})^*$ (eV)
ScF <sub>3</sub>	12.3
(NH <sub>4</sub> ) <sub>3</sub> ScF <sub>6</sub>	12.1
Sc <sub>2</sub> O <sub>3</sub>	11.5
ScCl <sub>3</sub>	10.5
Sc <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	8.0
TiF <sub>3</sub>	13.0
TiF <sub>4</sub>	14.7
TiO <sub>2</sub>	13.2

\* Frost *et al* (1976).

[O ( $2p$ )  $\rightarrow$  Ti ( $e_g$ )] transition. Kim and Winograd (1975) showed that the intensity of  $3e_g \rightarrow 4e_g$  charge-transfer satellite is larger compared to  $1t_{2g} \rightarrow 2t_{2g}$  [O ( $2p$ ) - Ti ( $t_{2g}$ )] transition. Accordingly, we have assigned the satellites in 10–15 eV range in all the oxides to the  $3e_g \rightarrow 4e_g$  transition.

From table 1 and figures 1 and 2, we see that the energy separation between the satellite and the main  $2p$  peak increases as we go from CaO to V<sub>2</sub>O<sub>5</sub> in the case of  $3d^0$  oxides and from SrO to Nb<sub>2</sub>O<sub>5</sub> in the case of  $4d^0$  oxides. We feel that this is due to the increase in the oxidation state or the charge of the metal. It might be expected that as the oxidation state increases, the occupied metal  $3d$  orbital becomes more stable giving a smaller satellite separation. However, increased charge on the metal ion is not expected to greatly affect the unoccupied metal  $e_g(4e_g)$  orbital whereas occupied O ( $2p$ ) ligand orbital ( $3e_g$ ) will be stabilised more leading to higher satellite separation. Many other transition metal compounds also show this trend as shown in table 2. Decrease of satellite separation in Sc<sup>3+</sup> compounds with the decrease in the charge of the metal ion is clear from the data. Similarly, satellite separation is lower in TiF<sub>3</sub> compared to that in TiF<sub>4</sub>. Increase in satellite separation in TiF<sub>4</sub> compared to ScF<sub>3</sub> is also obvious. Except for copper halides, all the other transition metal halides show an increase in the satellite separation with increase in charge on the metal ion (Robert 1975).

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