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Electron Spectroscopy

HeI PHOTOELECTRON SPECTRA OF CONDUCTING TRANSITION METAL OXIDES*

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High resolution HeI photoelectron spectra of TiO, VO, NbO, Ti_2O_3, Ti_3O_5, $Ti_{1\cdot96}V_{0\cdot04}O_3$ and $La_xSr_{1-x}CoO_3$ have been investigated. A sharp Fermi edge is observed in the valence band spectra of the metallic oxides, TiO, VO and NbO. The edge is also seen in the metallic phases of Ti_2O_3 and Ti_3O_5 above their semiconductor-metal transition temperatures. A new band is observed at E_F in the HeI spectrum of metallic $La_{0\cdot5}Sr_{0\cdot5}$ CoO_3.

Keywords: UV Photoelectron Spectra; Semiconductor-Metal Transitions; Fermi Edges in Metallic Oxides

INTRODUCTION

HIGH resolution UV photoelectron spectra of metals clearly show the presence of a sharp Fermi edge in the valence band region. Relative variations of work functions of metals have been measured by examining the Fermi edges in photoelectron spectra (Evans, 1973). Photoelectron spectrometers are calibrated with reference to the Fermi edge of gold. In this laboratory, transition metal oxides have been investigated extensively by employing XPS, UVPS as well as Auger spectroscopy (Rao *et al.*, 1979, 1980; and Sarma & Rao, 1980). Oxides such as V_2O_3 and Ti_2O_3 showing semiconductor to metal transitions have also been studied in this laboratory by employing UVPS and XPS (Rao *et al.*, 1979; and Vasudevan *et al.*, 1978). We considered it interesting to study metallic oxides such as TiO, VO and NbO with a view to see if Fermi edges can be seen in these systems in high resolution HeI photoelectron spectra. Following Beatham *et al.* (1980), we have examined semiconductor-metal (S-M) transitions (Mott, 1974; and Rao & Subba Rao, 1974) in Ti_2O_3 and Ti_3O_5 to see if the metallic phases show the Fermi edge in valence band spectra. We have compared the valence band spectrum of the high-temperature metallic phase of Ti_2O_3 with that of $Ti_{1\cdot96}V_{0\cdot04}O_3$ which is metallic at room temperature (Chandrashekhar *et al.*, 1970). Another system that has been examined is $La_{1-x}Sr_xCoO_3$ which becomes metallic when $x = 0.5$ (Bhide *et al.*, 1975).

EXPERIMENTAL

HeI photoelectron spectra were recorded with a ESCA-3 Mark II Spectrometer of V. G. Scientific Ltd., U. K. The oxides were prepared by procedures described in

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the literature. Sample purity was checked by comparing the core level binding energies with values reported in the literature. The spectrometer was operated under high resolution by keeping the pass energy of the analyser at 2 eV.

Results and Discussion

HeI spectra of the oxide metals TiO, VO and NbO are shown in Fig. 1. We clearly see the sharp Fermi edge similar to that exhibited by conventional metals like Cu and Au (Fig. 2).

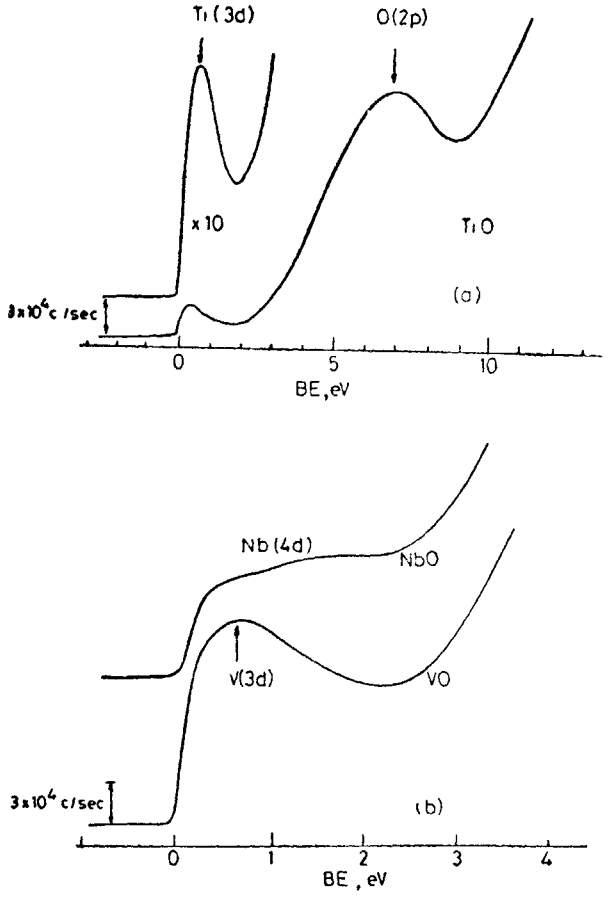

FIG. 1. HeI photoelectron spectra of (*a*) TiO (*b*) VO and NbO.

In Fig. 3, we show HeI spectra of Ti_2O_3 below and above the S-M transition temperature. In the same figure, the spectrum of metallic $Ti_{1\cdot96}V_{0\cdot04}O_3$ is also shown. In the solid solution, a clear edge is seen at room temperature, consistent with its metallic nature. In Ti_2O_3, the Fermi edge develops above the S-M transition temperature as can be seen from spectrum at 470 K. HeI spectrum of the high

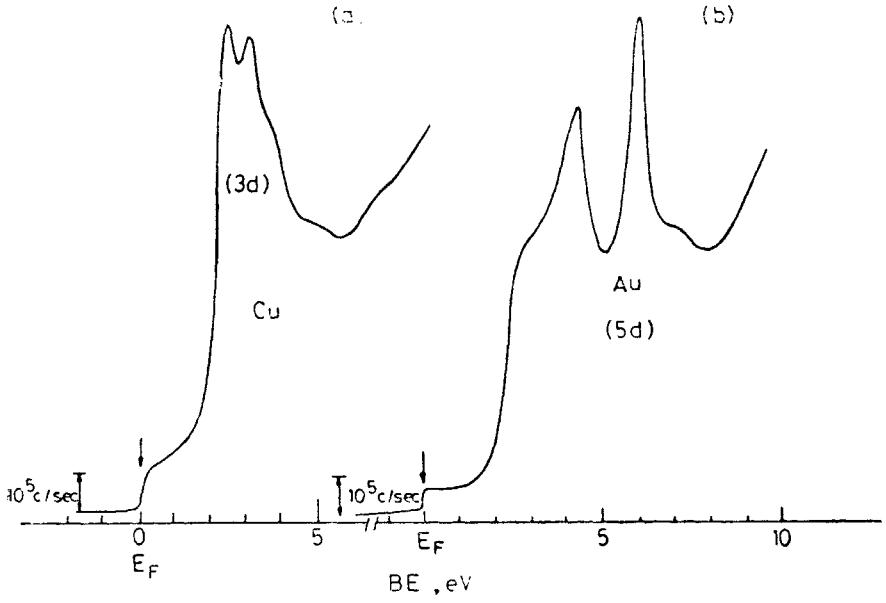

FIG. 2. HeI spectra of (*a*) Cu and (*b*) Au.

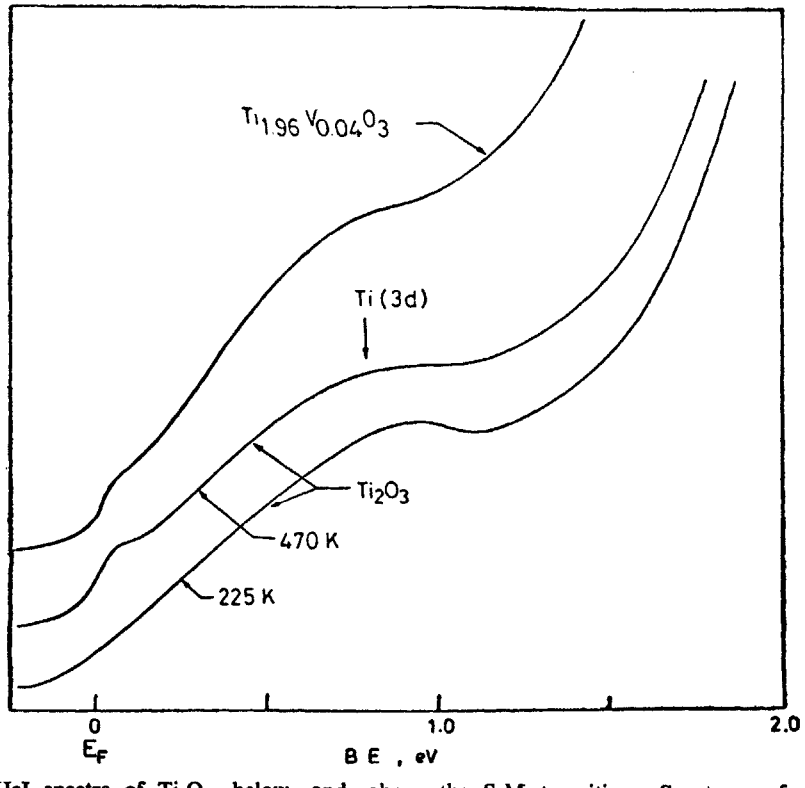

FIG. 3. HeI spectra of Ti_2O_3 below and above the S-M transition. Spectrum of metallic $Ti_{1.96}V_{0.04}O_3$ at 300 K is also shown.

temperature phase of Ti_2O_3 is indeed comparable to that of the room-temperature phase of the metallic solid solution. The S-M transition in Ti_3O_5 is accompanied by the emergence of the Fermi edge in the high-temperature phase (Fig. 4).

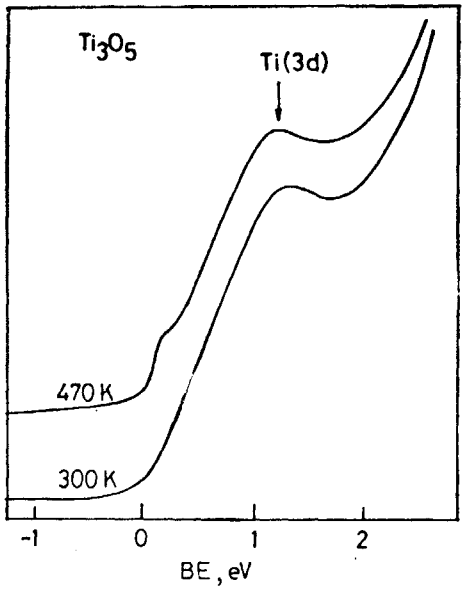

FIG. 4. HeI UPS of Ti_3O_5 below and above S-M transition.

The observations made here are consistent with the band models proposed by Goodenough (1971) in the case of TiO, VO and NbO as well as Ti_2O_3. The sharp Fermi edges are seen only in the HeI spectra because the spectrometer is operated at high resolution (< 0.1 eV) and the line-width of HeI radiation is much smaller than the instrument resolution.

Recently, Beatham *et al.* (1980) have investigated HeI spectra of VO_2 and V_2O_3 below and above their insulator-metal transition temperatures. In the metallic phases, they observe sharp E_F consistent with the metallic behaviour. A high resolution XPS study of metallic IrO_2 by Wertheim and Guggenheim (1980) shows a sharp cutoff at E_F and the calculated density of states is comparable to the XPS valence band spectrum. He II spectra of RuO_2 (Beatham & Orchard, 1979) also shows the sharp metallic edge, consistent with its metallic property.

The HeI spectrum of metallic $La_{0.5}Sr_{0.5}CoO_3$ shows a new band at E_F which is absent in insulating $La_{1.95}Sr_{0.05}CoO_3$ as shown in Fig. 5. This is expected according to the band model proposed in the literature (Raccah & Goodenough, 1968; and Bhide *et al.*, 1975) where it has been indicated that the $t_{2g}(\beta)$ with 2.5 occupancy provides the conduction band and is separated from the $t_{2g}(\alpha)$ level. So we attribute the new band to $t_{2g}(\beta)$ level in contrast to only one t_{2g} 6 band in $La_{1.95}Sr_{0.05}CoO_3$.

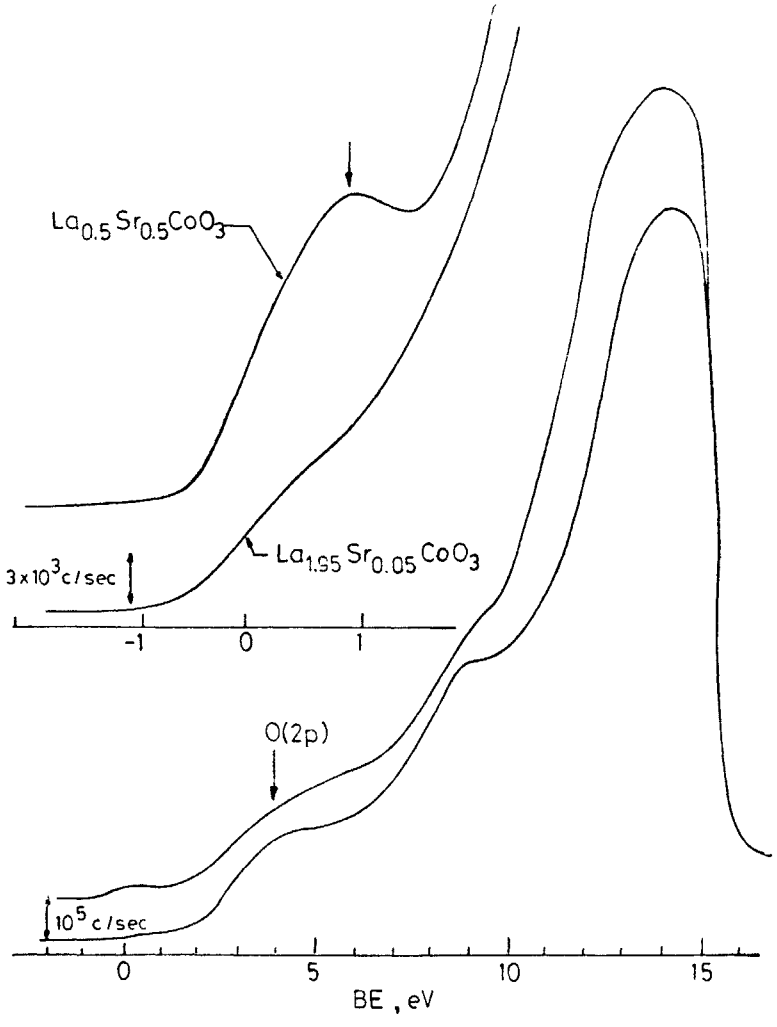

FIG. 5. HeI spectra of $La_{1.95}Sr_{0.05}CoO_3$ and $La_{0.5}Sr_{0.5}CoO_3$.

We do not observe a sharp Fermi edge here as in TiO, VO and other metallic oxides probably due to the narrow conduction band and low electron density at E_F. Several UVPS studies of organic compounds which show metallic behaviour have been reviewed by Grobman and Koch (1979). Absence of the Fermi edge in the organic metals is attributed to the low electron density at E_F unlike in inorganic metals and metallic oxides.

Appearence of a new band in the XPS of metallic Na_xWO_3 has been reported by Campagna *et al.* (1975). WO_3 which is an insulator does not show a 5*d* band whereas metallic Na_xWO_3 exhibits a sharp band at E_F. Hochst *et al.* (1980) have shown that the intensity of the 5*d* band in Na_xWO_3 increases markedly when $x > 0.28$.

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