

X-ray photoelectron and Auger studies of $\text{Ag}_{2+\delta}\text{S}$ †

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Abstract. The metal-insulator transition induced by changing the stoichiometry (δ) in $\text{Ag}_{2+\delta}\text{S}$ has been investigated employing x-ray photoelectron and Auger electron spectroscopies. Changes in the valence band structure in x-ray photoelectron are found to reflect the conductivity behaviour in these samples. The valence bands have been examined in a novel fashion by interatomic transitions in x-ray induced Auger spectra.

Keywords. X-ray photoelectron spectra; Auger electron spectra; silver sulfide; metal-insulator transition.

1. Introduction

Photoelectron spectroscopy has been found to be effective in studying metal-insulator transitions in transition metal oxides (Vasudevan *et al* 1978; Rao and Sarma 1982). It has been shown that the binding energies of the valence band peaks as well as the core levels shift as the temperature is changed through the transition temperature (Rao and Sarma 1982). Since UV photoelectron spectroscopy probes the valence band region with a high resolution, it has been possible to examine subtle changes in the shape of the band near the Fermi energy (E_F) across the transitions; HeI spectra of transition metal oxides such as V_2O_3 and VO_2 show a sharp cut-off in the photoemission intensity at the Fermi energy in the metallic phase (Rao and Sarma 1982; Beatham *et al* 1980).

Silver chalcogenides exhibit interesting metal-insulator transitions as a function of the stoichiometry (Shukla *et al* 1981; Shukla and Schmalzried 1979). Although detailed investigations of the transitions have been carried out using electrical and other measurements (Shukla *et al* 1981; Shukla and Schmalzried 1979; Vasan and Shukla 1981; Shukla *et al* 1982), no electron spectroscopic investigation of these systems has been reported to date. We therefore considered it useful to investigate the metal-insulator transition in the $\text{Ag}_{2+\delta}\text{S}$ system as a function of the stoichiometry, δ , employing x-ray photoelectron spectroscopy (XPS) as well as Auger electron spectroscopy.

2. Experimental

$\text{Ag}_{2+\delta}\text{S}$ was prepared by direct solid state reaction of pure silver powder (Johnson Matthey) and sulphur (Alpha Inorganic) *in vacuum* at 400°C. The specimens with

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various stoichiometry (different δ values) were prepared by solid state coulometric technique (Shukla *et al* 1981). The cell used for this purpose can be denoted as Ag/AgI/Ag_{2+ δ} S/Pt. Two samples were prepared, one with $\delta = 0.007 \times 10^{-3}$ (nearly stoichiometric composition, referred to in the text as the sample with $\delta = \delta^{\circ}$) and the other with $\delta = 2 \times 10^{-3}$ (silver excess composition referred to in the text as the sample with $\delta = \delta^*$).

X-ray photoelectron and x-ray induced Auger spectra were recorded using an ESCA 3 Mark II spectrometer of V.G. Scientific Ltd., U.K. The spectrometer has been described elsewhere (Rao *et al* 1979). As this spectrometer is provided with twin anode, both AlK α (1486.6 eV) and MgK α (1253.6 eV) radiations were used for unambiguous assignments of XPS and AES. However, the spectra reported here are taken with MgK α , as it offers lower natural width of the excitation source, compared to AlK α .

The samples of Ag_{2+ δ} S were freshly cleaned just before the sample introduction into the vacuum to minimize surface contamination. Ar⁺ etching was entirely avoided as it reduces the sample surface.

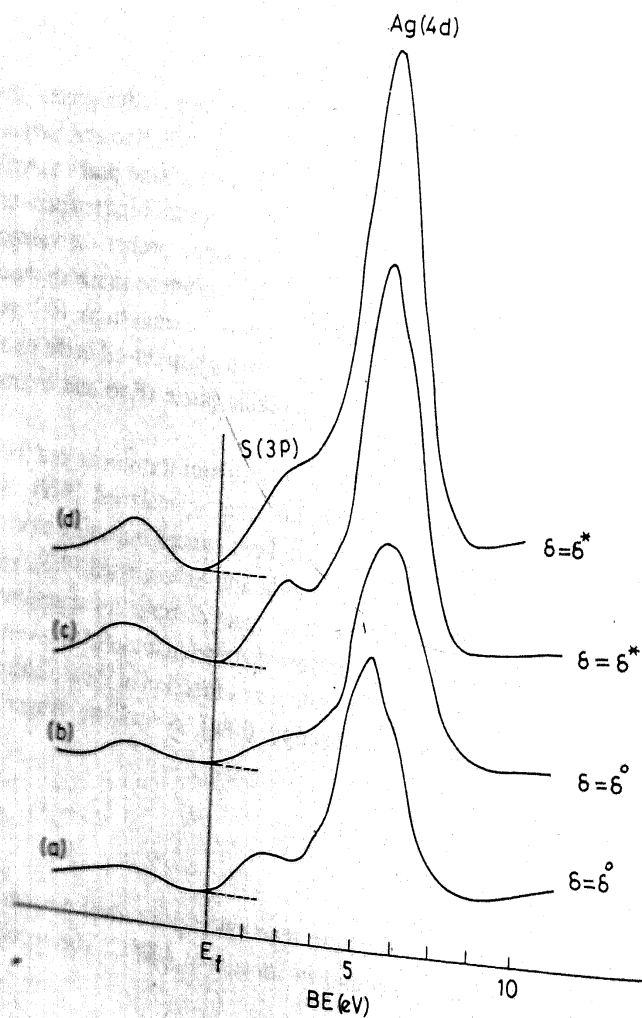


Figure 1. X-ray photoelectron spectra of the valence band in: (a) Ag_{2+ δ} S ($\delta = \delta^{\circ}$) at 295 K; (b) Ag_{2+ δ} S ($\delta = \delta^{\circ}$) at 473 K; (c) Ag_{2+ δ} S ($\delta = \delta^*$) at 295 K; and (d) Ag_{2+ δ} S ($\delta = \delta^*$) at 473 K.

3. Results and discussion

XPS valence bands of the two samples of $Ag_{2+\delta}S$ (with $\delta = \delta^\circ$ and $\delta = \delta^*$) are shown in figure 1 at temperatures above and below the transition temperature (449 K). We see that the $S(3p)$ derived band in the low-temperature α -phase of both the samples show a well-defined peak around 2 eV characteristic of a localized band. These peaks have no intensity at E_F indicating that the bands are localized well below the Fermi level in these insulating phases. This band becomes considerably broader in the high-temperature β -phase. The high-temperature phase with $\delta = \delta^\circ$, while showing considerable broadening of the $S(3p)$ derived band, does not have any intensity at the Fermi energy, corroborating the semiconducting behaviour of this sample at high temperatures. However, the sample with $\delta = \delta^*$, not only shows a distinct broadening of the topmost occupied valence band, but also has finite intensity at E_F as should be expected due to its metallic behaviour.

No significant change is found in binding energies of core levels (in XPS) with composition and temperature. The silver core level spectra of these compounds show negative chemical shifts with respect to those of silver metal, as reported earlier by Romand *et al* (1978). This negative chemical shift varies between -0.2 and -0.4 eV depending on the stoichiometry and temperature.

X-ray induced Auger signals due to the $Ag(M_{45}N_{45}N_{45})$ transition are seen in the 345–360 eV kinetic energy range (figure 2). Weak intensity features are seen at higher kinetic energies due to interatomic $M_{45}(Ag)VV$ process where V represents a $S(3p)$ derived band. We see from figure 2 that the onset of this interatomic structure differs depending on the stoichiometry and temperature. The Auger energy of a MVV transition is given by,

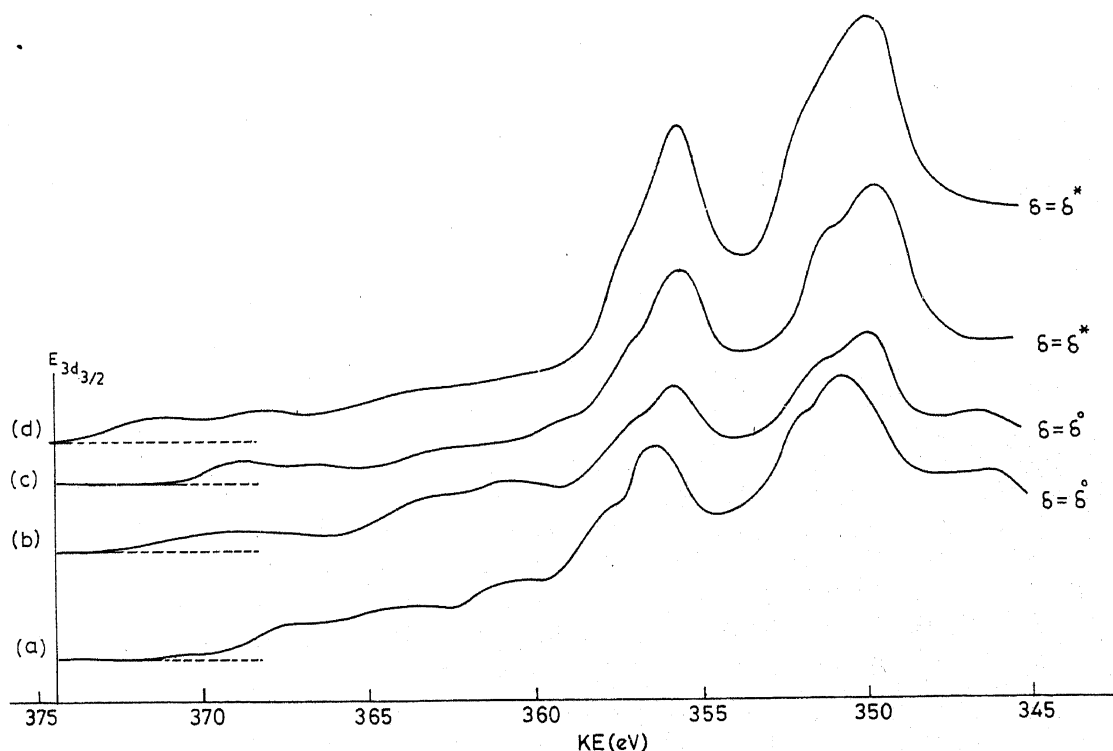


Figure 2. X-ray induced Auger electron spectra of the $Ag(M_{45}N_{45}N_{45})$ region in: (a) $Ag_{2+\delta}S$ ($\delta = \delta^\circ$) at 295 K; (b) $Ag_{2+\delta}S$ ($\delta = \delta^\circ$) at 473 K; (c) $Ag_{2+\delta}S$ ($\delta = \delta^*$) at 295 K; and (d) $Ag_{2+\delta}S$ ($\delta = \delta^*$) at 473 K.

$$E_{M\bar{V}\bar{V}} = E_M - 2E_V - U_{\text{eff}} \quad (1)$$

where E_M and E_V are the binding energies of the corresponding levels and U_{eff} is a term arising out of hole-hole interaction (in the final state of the valence band) and various polarization effects. Thus, the highest energy $E_{M\bar{V}\bar{V}}^{\text{max}}$ of $M\bar{V}\bar{V}$ transition is achieved when the valence electron is at E_F ($E_V = 0$) and U_{eff} is equal to zero; in such a situation, $E_{M\bar{V}\bar{V}}^{\text{max}}$ is equal to E_M . In this sense, E_M may be taken to be the counterpart of E_F in Auger transitions. We have therefore indicated the energy $E_{3d_{3/2}}$ in figure 2.

Since the core level binding energies do not change in this system, E_M in equation (1) would remain unchanged. Figure 1 reveals that the mid-points of the $S(3p)$ derived bands in all the cases remain essentially constant. Broadening of this band at high temperatures is not likely to cause a drastic modification in the $M\bar{V}\bar{V}$ transition, as the band gap in the insulating phase is small (< 1 eV) (Shukla and Schmalzried 1979). Changes in $E_{M\bar{V}\bar{V}}$ have therefore to be attributed to changes in U_{eff} . In such a situation, the occurrence of the onset of the interatomic structure at lower kinetic energies (~ 3.5 eV from the $3d_{3/2}$ energy) in the low temperature phases of both the samples (see figure 2) can be attributed to a considerably high U_{eff} . This indicates that in these cases, the $S(3p)$ derived band is a localized band forcing the two holes to be in close proximity. High temperature spectra of the sample with $\delta = \delta^\circ$ show the onset of the interatomic transition around 2 eV from $E_{3d_{3/2}}$ indicating a considerably broader band; a finite U_{eff} would however still indicate a localized band in accordance with the semiconducting nature of the sample even at high temperatures. The high temperature spectrum of the sample with $\delta = \delta^*$, on the other hand, shows a rise in intensity at $E_{3d_{3/2}}$ indicating that U_{eff} is nearly equal to zero in this case. This observation confirms the delocalized (metallic) behaviour of the $\text{Ag}_{2+\delta}\text{S}$ sample with $\delta = \delta^*$ at high temperature.

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