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XPS Spectra of Some Transition Metal and Alkaline Earth Monochalcogenides*

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The first-row transition-metal monosulfides and alkaline-earth chalcogenides were studied by means of X-ray photoelectron spectroscopy. It is shown that the bonding in the alkaline earth compounds is relatively ionic with XPS evidence for significant charge separation. On the other hand, transition metal sulfides, with the exception of MnS, appear to be principally metallic with little or no charge separation. Values for the inner orbital binding energy shifts are reported for a large number of monochalcogenides.

Introduction

The solid-state chemistry of transition-metal sulfides has been extensively investigated, and on the basis of structural correlations (*1–3*) it has been concluded that metallic interactions are important in the bonding in the solids. The development of photoelectron spectroscopy has provided a tool for the semiquantitative investigation of the extent of charge separation in solids (*4*), and X-ray photoelectron spectroscopy has been used in a study of the electronic structure of vanadium-deficient vanadium monosulfide with the NiAs-type structure (*5*). This study provided an experimental confirmation of the proposed covalent nature of the bonding in $V_{0.92}S$, and motivated a further investigation of the monosulfides of the first-row transition metals. In order to provide a basis for comparison, some alkaline-earth monochalcogenides and transition-metal monoxides were also examined. The compounds for which results are reported are: MgX, CaX, and SrX with $X = $ O, S, Se; TiY and MnY with $Y = $ O, S; and VS and $Sc_{1-x}S$.

Experimental

The monochalcogenides were prepared by high-temperature annealing of materials which were initially prepared by the direct combination of high-purity elements in Vycor or fused-silica tubes at temperature below 700°C. The high-temperature annealing was carried out in inductively heated tungsten containers with lids containing small orifices. The final annealing temperatures were sufficiently high to assure homogenization and distillation of volatile impurities (1300–1500°C). The monochalcogenides were characterized by powder X-ray diffraction using the Debye–Scherrer technique. The lattice parameters obtained for the various phases are reported in Table I.

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TABLE I

Compound	Crystal structure type	Lattice parameters (Å)
MgS	NaCl	$a = 5.2024 \pm 0.001$
MgSe		$a = 5.462 \pm 0.001$
CaS		$a = 5.695 \pm 0.002$
CaSe		$a = 5.9327 \pm 0.0001$
SrS		$a = 6.1040 \pm 0.0015$
SrSe		$a = 6.2289 \pm 0.0014$
$ScS_{1.01}$		$a = 5.192 \pm 0.001$
$ScS_{1.24}$		$a = 5.165 \pm 0.001$
$TiO_{1.14}$		$a = 4.176 \pm 0.001$
TiS	NiAs	$a = 3.3067 \pm 0.0001$ $c = 6.3725 \pm 0.0001$
$VS_{1.04}$	MnP	$a = 5.854 \pm 0.007$ $b = 3.304 \pm 0.007$ $c = 5.820 \pm 0.002$
MnO	NaCl	$a = 4.441 \pm 0.002$
MnS		$a = 5.201 \pm 0.001$

The initial set of XPS measurements was made using transition-metal monochalcogenide samples that were prepared using Vycor tubing which had not been outgassed for the reaction of the elements and with exposure of the samples to the laboratory atmosphere between steps of the synthesis. The X-ray photoelectron spectrometer, a McPherson ESCA 36, was at this time equipped with a glove box, but this box did not have an evacuable entry port. As a consequence of the above-stated conditions oxide peaks, as well as peaks attributable to the sulfides, were observed in the spectra of $Sc_{1-x}S$, TiS, VS, and MnS, and mixtures of oxide spectra were observed for TiO, VO, and MnO. The spectrum observed for bulk VO was so broadened and overlapped as to make the assignment of a vanadium $2p$ binding energy for V in VO highly uncertain and accordingly no value for this binding energy is reported.

The second series of measurements was carried out on the alkaline-earth chalcogenides which were prepared in outgassed (to 10^{-6} Torr at 500°C) fused-silica tubes prior to high-temperature annealing and which were exposed only to dry box atmospheres between steps in the preparation. The final exposures, upon introduction to the spectrometer, were in a dry box, attached to the spectrometer sample region via an O-ring flange, which maintained a measured H_2O concentration of less than 6 ppm.

In spite of these precautions, the monotellurides of Mg, Ca, and Sr, which were observed to discolor in the dry box atmosphere, yielded spectra characterized by at least three different shifts in the tellurium $4d$ binding energy, indicating oxidized tellurium. The observed Mg, Ca, and Sr shifts were accordingly suspected of being characteristic of oxides (and were of the appropriate magnitudes to be so considered) and thus are not reported here.

The values of the binding energies of the transition-metal monochalcogenides, which are generally rather highly conducting solids, were measured relative to the Fermi energies of the solids when in contact with the spectrometer sample holder. The binding energies of the alkaline-earth chalcogenides, on the other hand, were determined relative to the Fermi energy of gold in contact with the sample holder by subtracting the shifts of the $4f$ levels of gold which had been vapor-deposited in extremely small quantities onto the surface of the sample (*6*, *7*).

The spectra were observed as composites of ten 111 point scans (1 sec/point over 20-eV intervals, except for the gold $4f$ calibration measurements which were made over a 10-eV interval). The X-rays were provided by a MgK_α source. During the measurements, the spectrometer was pumped by a turbomolecular pump to a residual pressure of about 2×10^{-7} Torr and the sample region was differentially pumped by a standard helium cryopump. Several characteristic spectra, from which X-ray satellites have been removed, are shown in Fig. 1.

Results and Discussion

The values observed for the sulfur $2p_{3/2}$ binding energies in the alkaline-earth monosulfides are reported in Table II. These values

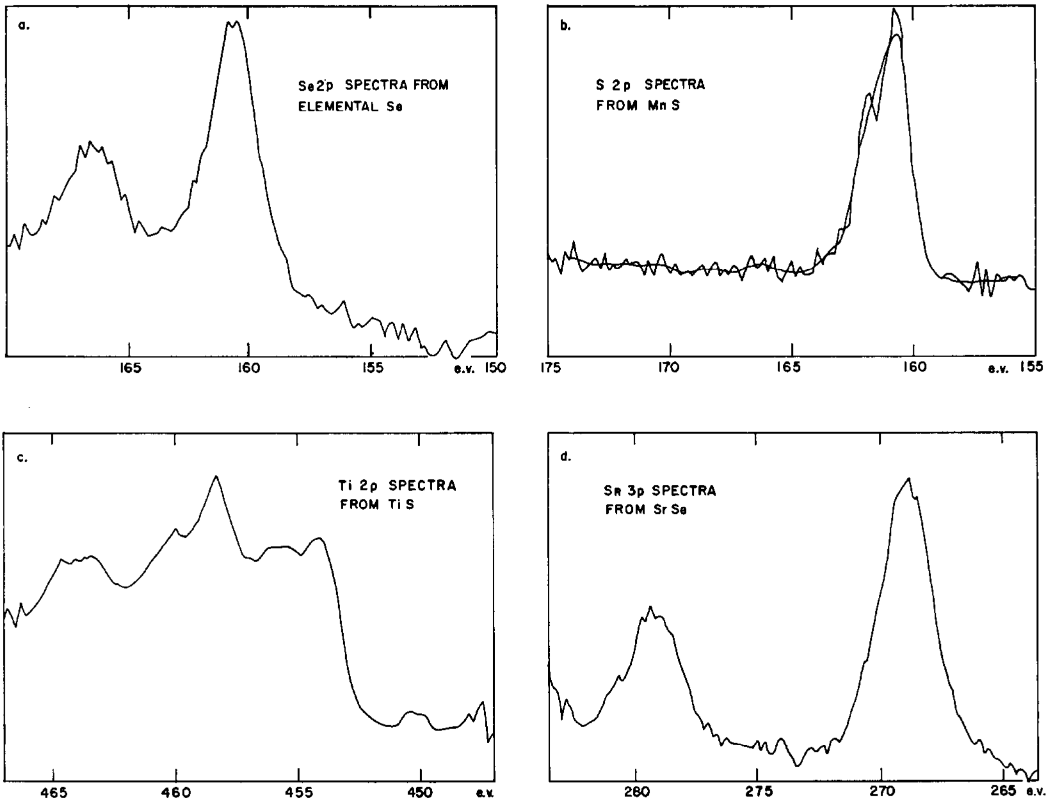

FIG. 1. (a) Se $2p_{1/2}$ and $2p_{3/2}$ peaks from elemental Se. The values along the abscissa are relative to the gold Fermi energy. (b) S $2p$ peaks from S in MnS. Unsmoothed curve shows the spin–orbit coupling. (c) Ti $2p$ peaks from TiS. The multitude of peaks presumably results from surface oxidation. The peak with lowest binding energy is taken as characteristic of Ti in TiS. (d) Sr $3p_{1/2}$ and $3p_{3/2}$ spectra from SrSe.

are the same within experimental error and the average value, 160.85 eV, is in excellent agreement with the value 160.8 eV reported Swartz *et al.* (*8*) for Na_2S. Thus the value of 160.8 eV is very well established as the value of the sulfur $2p_{3/2}$ binding energy for compounds in which sulfur is combined with the most electropositive elements. This value may be compared with the value reported for elemental (unshifted) sulfur (*8*) (162.2 eV) and the value reported by Franzen and Sawatzky (*5*) for sulfur in $V_{0.92}S$ (162.0 eV).

TABLE II

S $2p_{3/2}$ AND Se $3p_{3/2}$ BINDING ENERGIES MEASURED RELATIVE TO THE FERMI ENERGY OF Au

Compound	Binding energy (eV)
MgS	160.8 ± 0.2
CaS	161.0 ± 0.2
SrS	160.75 ± 0.2
MgSe	159.95 ± 0.2
CaSe	159.1 ± 0.2
SrSe	159.1 ± 0.2

The constancy of the values for the binding energies of the S ($2p_{3/2}$) orbital electrons in MgS, CaS, and SrS may be somewhat accidental. Corrections for the madelung potentials certainly are not the same for the three compounds. In addition, all three compounds are certainly not all equally ionic or covalent. It is possible that these two effects tend to cancel each other. Although corrections for madelung potentials have been attempted

(*9*), no sufficiently thorough study has yet been accomplished in connection with the electrical charging of the sample to establish its use in deriving quantitative information concerning ionic–covalent bonding from XPS. This problem has been investigated recently (*10*); the results are encouraging, but they are not sufficiently complete to be used herein. Similar statements apply to the selenides and to a given cation in a series of monochalcogenides.

The values of the sulfur $2p_{3/2}$ binding energies in ScS, TiS, and VS are reported in Table III. The value obtained here for VS is in good agreement with that previously reported (162.0 eV) (*5*). The values of Table III are the same within experimental error (162.35 ± 0.20 eV), are substantially greater than the value for sulfur in its most ionized state, and are the same (within experimental error) as the value reported by Swartz *et al.* (*8*) for elemental sulfur. Thus the transition-metal monosulfides are significantly less ionic in character than the alkaline-earth monosulfides, indicating that the electrons are extensively delocalized into the transition-metal $3d$ orbitals. This conclusion, appropriate for ScS, TiS, and VS, is in agreement with that previously reached for VS alone in the study of the XPS of $V_{0.92}S$ (*5*).

TABLE III

S $2p_{3/2}$ BINDING ENERGIES MEASURED RELATIVE TO THE FERMI ENERGY OF THE COMPOUND

Compound	Binding energy (eV)
$ScS_{1.24}$	162.1 ± 0.2
$ScS_{1.01}$	162.45 ± 0.2
TiS	162.3 ± 0.2
VS	162.3 ± 0.2
MnS	160.8 ± 0.2

TABLE IV

METAL $2p_{3/2}$ BINDING ENERGIES MEASURED RELATIVE TO THE FERMI ENERGY OF THE COMPOUND

Compound	Binding energy (eV)
$ScS_{1.01}$	401.7 ± 0.4
TiO	454.7 ± 0.2
TiS	454.2 ± 0.2
VS	512.7 ± 0.2
MnO	641.3 ± 0.2
MnS	640.45 ± 0.2

The value obtained for the sulfur $2p_{3/2}$ binding energy in MnS (160.8 ± 0.20 eV) is distinctly lower than that found for the other transition-metal monosulfides studied here, indicating that MnS is more ionic in character (there is less delocalization of electrons into Mn $3d$ orbitals) than is the case for the early first-row transition-metal monosulfides. This observation is undoubtedly correlated (*3*) with the fact that the MnS is of the NaCl-type structure (as opposed to MnP-type for VS and NiAs-type for TiS) and with the known high-spin paramagnetic susceptibility of α-MnS.

The binding energies of the $2p_{3/2}$ electrons in the transition metals in the monosulfides and, where observable, the monoxides are reported in Table IV. Where comparison is possible, i.e., between Ti in TiS and in TiO and between Mn in MnS and in MnO, it is found that the binding energy in the sulfide is lower than that in the oxide, again indicating a decreased ionic nature of the bonding in the sulfides compared with the oxides.

The binding energies found for selenium $3p_{3/2}$ electrons in the alkaline earth monoselenides are reported in Table I. The values obtained for CaSe and SrSe are in excellent agreement and probably represent a good value for selenium in its most anionic state. This value, 159.15 ± 0.20 eV, is substantially lower than the value reported by Swartz *et al.* (*8*) for selenium in ZnSe (159.7 ± 0.2 eV) indicating a smaller charge separation in ZnSe than in the alkaline-earth monoselenides, a not unexpected result. The binding energy for elemental selenium (relative to gold) found here is 160.9 ± 0.2 eV. This value is not in agreement with the value reported by the previous workers (159.9 ± 0.2 eV) (*8*). The $3p_{3/2}$ binding energy for selenium in MgSe reported in Table I is surprisingly large and should be reevaluated before an interpretation is proposed.

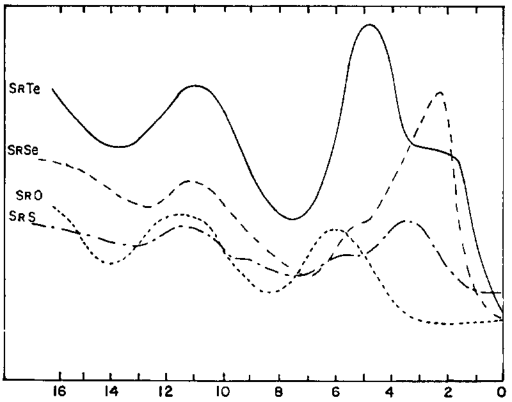

FIG. 2. The valence band regions of the strontium monochalcogenides showing the expected decrease in binding energy with increased atomic number. Intensity units are arbitrary and the binding energies are in electron volts.

Figure 2 shows the four spectra of the strontium chalcogenides in the valence band region. Three features observed in this spectral region are worthy of note: (1) a peak at about 11 eV observed in all four spectra, (2) a peak at 5–6 eV observed primarily in SrO and SrTe, and as a weak side peak in SrS and SrSe, and (3) a peak at lowest binding energy with peak position dependent upon the nature of the chalcogen anion.

The peak at about 11 eV is apparently characteristic of Sr and is presumed to be due to secondary processes.

The peaks at energies in the range 5–6 eV are probably due to oxygen, with the side peaks in this region in the sulfide and selenide cases resulting from a minor impurity, and the large, broad peak in the telluride case presumably originating from oxygen in combination with both strontium and tellurium, as discussed previously.

The peaks at lowest energy would then be ascribed principally to the valence p shells of the respective chalcogens, and the order of binding energies $O > S > Se > Te$ would follow from the accepted difference in electronegatives of the elements. This ordering observed in the lowest binding peaks for all of the alkaline-earth monochalcogenides, and the binding energies accordingly assigned to the various valence p levels are: O, 6.1 ± 0.5; S, 3.2 ± 0.4; Se, 2.4 ± 0.2 (elemental selenium provided two peaks, an oxygen peak at 6.0 ± 0.4 eV and a selenium peak at 2.2 ± 0.2 eV); Te, 2.1 ± 0.5 eV.

Conclusions

The available XPS data for the monochalcogenides presented here strongly indicate that there are important covalent effects in the bonding of the early first-row transition-metal monosulfides. This conclusion is in agreement with the well-accepted view of bonding in the NiAs-type compounds as being rather highly covalent in character, but also seems to apply to ScS with the rock-salt-type structure. The new data provide the following characteristic binding energies:

(1) S $2p_{3/2}$: in strongly ionic sulfides (160.85 ± 0.20 eV), in conducting compounds (162.35 ± 0.20 eV);

(2) Ca $2p_{3/2}$: in strongly ionic compounds (346.65 ± 0.20 eV);

(3) Sr $3p_{3/2}$: in strongly ionic compounds (269.25 ± 0.20 eV);

(4) Se $3p_{3/2}$: in elemental selenium (160.9 ± 0.2 eV) and in strongly ionic selenides (159.15 ± 0.2 eV).

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