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An X-Ray Photoelectron Study of $V_{0.92}S$ with the NiAs-Type Structure

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An X-ray photoelectron study of defect vanadium monosulfide reveals that this compound can be thought of as an intermetallic compound with relatively little charge transfer between vanadium and sulfur atoms. This conclusion is reached from a study of the core electron binding energies, as well as from the strong band mixing found for the conduction and valence bands.

Introduction

The NiAs-type structure, which has been described frequently as a hexagonal close packing of anions with cations in the trigonal antiprismatic holes, is found for a large number of transition-metal compounds, many of which exhibit properties that are generally metallic. The metallic properties (metallic conductivity, Pauli paramagnetism, negligible solubility in H_2O, metallic luster, etc.) of the compounds has led to the suggestion that the transition-metal *d*-orbitals are generally broadened to form a partially filled conduction band in these solids.

This model provides much insight into the properties of compounds with the NiAs structure type. However, attempts to refine this model have not led to any generally accepted improvements in understanding. One possible fundamental improvement of the model would be to provide information concerning the extent of interaction of the nonmetal 3-*p* band (the valence band) with the metal 3-*d* levels (the conduction band). It was with the purpose of providing experimental evidence concerning this interaction in vanadium monosulfide with the NiAs-type structure that the work reported here was undertaken.

Experimental

The vanadium monosulfide used in obtaining the X-ray photoelectron spectrum (XPS) was prepared from high purity (99.99%) sulfur and vanadium metal prepared and analyzed by groups at the Ames Laboratory of the USAEC, Ames, Iowa. The impurity levels in a vanadium bulk sample were found to be: Si, 300 ppm; O, 280 ppm; Al, 100 ppm; C, N, Ni, Fe, and Mg, all less than 60 ppm. Metal particles obtained from the bulk sample by filing were analyzed by a wet method and found to be 100.08% V, indicating that negligible contamination resulted from the filing. The metal particles were placed in a sealed, quartz tube together with a quantity of sulfur to yield $V/S = 0.92$, and the reaction mixture was held at 700°C for several weeks. The tube was opened in a N_2-filled glove box, and the sample was introduced from there directly into the XPS spectrometer without

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TABLE I

Energy level species	1*s* eV	2*s* eV	2*p*-$\frac{1}{2}$ eV	2*p*-$\frac{3}{2}$ eV
Vanadium metal			520.3 ± 0.3	512.7 ± 0.2
Vanadium in VO_2			523.4	515.8
Vanadium in $V_{0.92}S$		628.0 ± 0.2	520.1 ± 0.2	512.7 ± 0.2
Elemental sulfur		227.9 ± 0.1	164.7 ± 0.1	163.7 ± 0.1
Sulfur in $VS_{1.08}$		226.3 ± 0.2	163.0 ± 0.2	162.0 ± 0.2
Elemental oxygen	532			
Oxygen in sample	531.8 ± 0.2			

any contact with air. A portion of the sample was examined by the Guinier powder diffraction technique and was found to consist only of NiAs-type phase, as was expected from the method of preparation (*1*).

An AEI ES 200 (linewidth <0.7 e) spectrometer fitted with a Mg X-ray source was used for the XPS measurements. The sample was powdered and pressed into In foil, which was mounted on a copper sample holder. This method of treating powdered samples virtually eliminates charging effects. This is true even for highly insulating materials like SiO_2. The spectra were collected at –10°C and a vacuum of 5×10^{-9} Torr. Carbon and water build-up on the surface of the sample during the course of a measurement (6 hr) was eliminated by using a liquid nitrogen cooled cryopump. The data accumulated on a PDP8 computer with a 32 K disk storage. The zero of energy, E_F, was determined from both the Fermi level in Pt metal and from the 4*d* band of Ag which is 3.75 eV below the Fermi level.

In order to enable a proper comparison of the binding energies, spectra of vanadium metal, elemental sulfur and VO_2 were also collected. Spectra of clean V metal were obtained by argon ion etching the sample until the oxide peaks were virtually eliminated. VO_2 spectra were obtained from single crystals crushed in a N_2 filled glove box and pressed into In foil.

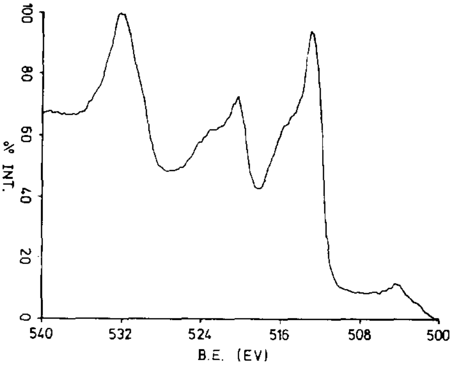

FIG. 1. XPS spectrum of the V2*p* and O1*s* electrons of $V_{0.92}S$. The binding energy of the O1*s* electrons corresponds to free oxygen or oxygen in H_2O.

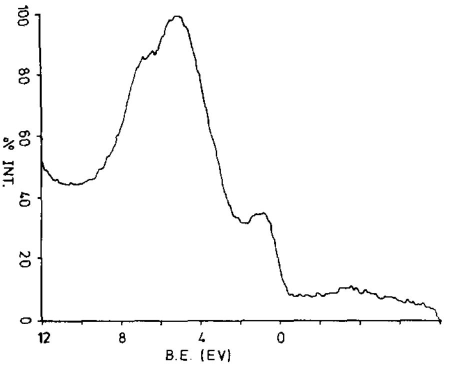

FIG. 2. XPS spectrum of the valence and conduction band region of $V_{0.92}S$. The zero of energy was determined from the Fermi level of Pt.

Results

The peak positions estimated from the computer produced graphs of intensity versus energy ($E_F = 0$) are tabulated together with their uncertainties in rows 1, 3, 4, 5, and 7 of Table I. The vanadium 2*p* peaks, together with the oxygen 1*s* peak, are shown in Fig. 1

and the conduction and valence bands are shown in Fig. 2.

Discussion

An examination of the spectrum indicates that the sample was not seriously contaminated with oxygen in the portion of the solid accessible to the ionizing radiation. The problem of oxygen contamination in the investigation by ESCA spectrometry of compounds such as VS is generally severe; thus, care is required to assure that observed peak positions are those characteristic of the compound of interest and that they are not seriously shifted by oxide formation. In this regard, the principal contribution to the oxygen 1*s* peak at 531.8 eV (see Fig. 1) is most probably from oxygen in a surface contaminant, but *not* from oxygen bound to vanadium, as can be seen from the negligible shift relative to elemental oxygen. The O^{2-} peak (as in VO_2) is shifted by about 1.4 eV relative to elemental oxygen, and there may be a small contribution to the 531.8 eV peak (Fig. 1) as a slight shoulder on the principal oxygen 1*s* peak.

Another indication that oxygen contamination (in the form of vanadium oxide) is, while present, not dominant in the spectrum, is the occurrence of relatively small shoulders on the V2*p* peaks at the positions expected for vanadium oxides (Fig. 1).

An examination of the spectrum suggests that there are no important instrumental grounding or charging effects which would raise doubts about the reported shifts. This follows from the fact that the Fermi level is observed to occur at 0 binding energy (Fig. 2). Thus, the shifts for V and S reported in the table are appropriate to the elements in the solid under study.

The spectrum of the conduction and valence band region of $V_{0.92}S$ (Fig. 2) is consistent with the generally accepted point of view that the higher lying states in this region are principally vanadium 3*d*-type states and the lower lying states are sulfur 3*p*-type states. The small relatively narrow peak at a binding energy of about 1 eV is probably virtually pure *d* band, whereas the broad peak between 2 and 8 eV most likely has a substantial sulfur *p* population with broadening due to hybridization with vanadium *s* and *p* orbitals (*2*).

The shifts in the binding energy of the vanadium 2*p* and the sulfur 2*s* and 2*p* electrons relative to the elements demonstrate that sulfur and vanadium in $V_{0.92}S$ are involved in very little charge transfer. The sulfur shifts are a more sensitive measure of charge transfer since, as has been demonstrated in extensive studies (*3*, *4*), the sulfur 2*p* level shifts by about 5 eV per charge, compared with about 0.6 eV per charge for V (*5*, *6*).

The observed 1.7 eV shift of the sulfur 2*p* levels in $V_{0.92}S$ thus corresponds to –0.4 units of charge on the sulfur ions. Such a charge would imply a similarly small positive charge on the vanadium ions, and, taking the oxides as purely ionic, to a shift of only 0.2 eV for the V 2*p* levels. Such a shift would be just within the experimental accuracy of the measurement, and is thus consistent with the observation that the vanadium 2*p* peak positions obtained from $V_{0.92}S$ and from vanadium metal are indistinguishable. In arriving at such conclusions we have neglected any lattice or crystal potential effects in so far as these may be different for the various compounds considered. Although this may cause errors, a study of the vanadium oxides seems to indicate that lattice effects are not dominant. That magnitude of the sulfur charge is considerably less than 2 can also be concluded from a comparison with the sulfur 2*p* binding energies in TaS_2 recently obtained in this laboratory (161.5 and 160.6 eV). Even if TaS_2 is assumed to be completely ionic a charge of only –1 is obtained for sulfur in VS.

This small charge on the sulfur atoms in $V_{0.92}S$ suggests that the model discussed in the introduction must be modified by strongly delocalizing the charge on the S^{2-} ions into orbitals centered on the vanadium ions, which can most straightforwardly be accomplished by mixing of sulfur 3*p* orbitals with the vanadium 3*d* orbitals, i.e., by mixing of the valence and conduction bands. Furthermore, the absence of a region of very low densities of states between the high energy peak in the conduction band and the lower energy valence

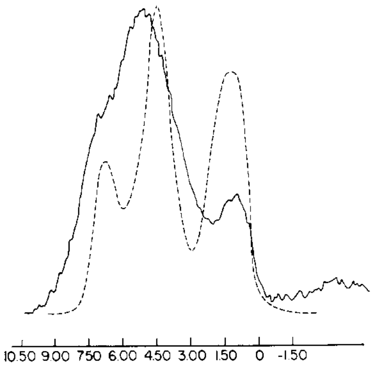

FIG. 3. The XPS spectrum of the valence and conduction band region corrected for background (full line) and the density of states obtained by England et al. convoluted with a Gaussian curve 0.8 eV in width vs. binding energy in eV.

band peaks shown in Fig. 2 indicates that, to within the inherent 0.7 eV resolution of the method, there is a strong mixing and overlap of the bands.

Conclusion

The X-ray photoelectron spectrum of a sample of $V_{0.92}S$ with the NiAs-type structure provides evidence that there is relatively little net charge transfer from vanadium to sulfur in the solid and that there is substantial mixing of the valence (principally *s*, 3*p*) and conduction (principally V, 3*d*) bands. These consistent observations suggest that the compound has the character of an intermetallic type compound, rather than that of an ionic compound with a transition-metal *d*-band.

This conclusion is in good agreement with the theoretical density of states obtained by England, Liu, and Myron (*2*) using the KKR method. The results of theory and experiment are compared in Fig. 3.

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