

Contribution from Ames Laboratory—DOE and Department of Chemistry, Iowa State University, Ames, Iowa 50011, and Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13901

X-ray Photoelectron Spectra and Bonding in Transition-Metal Phosphides

CLIFFORD E. MYERS,*† HUGO F. FRANZEN, and JAMES W. ANDEREGG

Received July 5, 1984

X-ray photoelectron spectra of solid ScP, TiP, VP, MnP, and FeP have been obtained in the valence-conduction band region and for the $2p_{3/2}$ core levels of both metal and phosphorus. The results show a regular increase in photoelectron intensity near the Fermi energy and a regular decrease in core level shifts relative to the elements across the series. These are interpreted as arising from a decreasing ionicity coupled with increasing metallic character accompanying the increasing number of metal d electrons.

Introduction

Many of the important properties of solid compounds depend on the nature and degree of interaction of orbitals at or near the valence level in the respective atoms (the so-called "frontier" orbitals). These properties include electrical and thermal conductivity, magnetic susceptibility, crystal structure, phase transitions, and thermodynamic stability. A principal goal of study of solids is achieving a deeper understanding of these orbital interactions and their effects on the above-mentioned properties. The development of photoelectron spectroscopy (ESCA) as a tool for studying solids has provided a means for investigating these interactions. Qualitative information on the density of states near the Fermi energy and on the formation of bands just below the Fermi energy can be gained by measurement of electron-binding energies in the valence and conduction band region of the photoelectron spectrum. Furthermore, investigation of core level shifts upon compound formation can give additional insight into the degree of metal-to-nonmetal electron transfer.

The recent extensive interest in the transition-metal phosphides and the close structural relationships between sulfides and phosphides of the first-row transition metals made a study of the phosphides attractive. These compounds provide an interesting evolution of structure type. ScP has the rock salt or NaCl-type structure¹ which is usually associated with ionic bonding, TiP has a structure that may be regarded² as consisting of alternating layers of the NaCl-type and the WC-type structures (the latter is closely related to the NiAs-type structure), VP has the NiAs-type structure,³ which is considered to be favorable for metal-metal bonding, CrP through CoP have the MnP-type structure,⁴ which is a distortion of the NiAs type, and NiP has a unique structure that shares some features with the MnP type but retains some significant differences.⁵

Scandium monophosphide has been described as metallic on the basis of augmented plane wave energy band calculations,⁶⁻⁹ although the results of at least one calculation show a reduction in the density of states at the Fermi surface compared to that of scandium metal.¹⁰ On the other hand, semiconducting behavior was suggested for ScP on the basis of an empirical correlation¹¹ and LCAO tight binding calculations,¹² and a band gap of 1.1 eV at room temperature has been reported for ScP epitaxially grown from the vapor on a silicon substrate.¹³ The monophosphides of the remaining first-row transition metals are all reported to be metallic,¹⁴ and this was confirmed by LCAO tight binding calculations on V, Cr, and Mn phosphides¹⁵ and by a self-consistent augmented plane wave calculation on MnP.¹⁶

The purpose of this work was an examination of the X-ray photoelectron spectra of first-row transition-metal monophosphides to assess the degree of mixing of metal and phosphorus orbitals from consideration of the valence and conduction region of the spectra and to gauge the degree of net metal-to-phosphorus electron transfer from shifts of core-level binding energies. Photoelectron spectra of some of the compounds reported in this work have been reported recently,^{17,18} and these will be compared with our results.

Table I. Preparation of Samples

nominal composition	final reacn temp, ^a °C	reacn time, days	X-ray results	ref ^b
ScP			ScP	1
TiP	900	30	TiP	2
VP	850	3	VP	3
MnP	850	3	MnP	4
FeP	900	2	FeP	4

^a Approximate. ^b References for structure data from which powder patterns were calculated.

Experimental Section

The samples were prepared by reaction of high-purity metals and red phosphorus in evacuated and sealed fused silica or Vycor tubes using procedures and precautions described elsewhere.^{19,20} The reactants were weighed and placed in the tubes within a glovebox having a purified nitrogen atmosphere. The tubes had been previously outgassed under high vacuum. Provision was made for transfer of the tubes between the vacuum system and the glovebox without exposure of their inner walls or contents to air. A summary of reaction conditions is given in Table I. The products were identified by their X-ray powder diffraction patterns, obtained by the Guinier or Debye-Scherrer methods, as compared to patterns calculated from crystallographic data given in the references listed in Table I.

The sample tubes were opened in a glovebox attached directly to the sample port of an AEI ESCA 200B photoelectron spectrometer. The glovebox was filled with continuously purified helium, and the O₂ and H₂O levels were below 1 and 0.5 ppm, respectively. After being crushed, the materials were mounted on the probe of the spectrometer by pressing the powders into a piece of indium foil.

The samples were etched in the spectrometer for 40-45 minutes with 5.0 kV Ar⁺ ions to remove surface layers not characteristic of the bulk material itself. Core level peaks clearly identified as characteristic of the bulk phosphides were observed to be unshifted by the etching process,

- (1) Parthe, E. *Acta Crystallogr.* **1963**, *16*, 71.
- (2) Snell, P. *Acta Chem. Scand.* **1967**, *21*, 1773.
- (3) Selte, K.; Kjelshus, A.; Andreson, A. F. *Acta Chem. Scand.* **1972**, *26*, 4057.
- (4) Rundqvist, S. *Acta Chem. Scand.* **1965**, *19*, 1006.
- (5) Larsson, E. *Ark. Kemi* **1965**, *23*, 335.
- (6) Switendick, A. C.; Jones, E. D. *Bull. Am. Phys. Soc.* **1968**, *13*, 365.
- (7) Wimmer, E.; Neckel, A.; Schwartz, K.; Eibler, R. *J. Phys. C* **1979**, *12*, 5453.
- (8) Dorrer, M.; Eibler, R.; Neckel, A. *Theor. Chim. Acta* **1981**, *60*, 313.
- (9) Eibler, R.; Dorrer, M.; Neckel, A. *Theor. Chim. Acta* **1983**, *63*, 133.
- (10) Jones, E. D. *Phys. Rev.* **1969**, *180*, 455.
- (11) Scalr, N. *J. Appl. Phys.* **1962**, *33*, 2999.
- (12) Perkins, P. G.; Marwaha, A. K.; Stewart, J. J. P. *Theor. Chim. Acta* **1981**, *59*, 555.
- (13) Yim, W. M.; Stofko, E. J.; Smith, R. T. *J. Appl. Phys.* **1972**, *43*, 254.
- (14) Hulliger, F. *Struct. Bonding (Berlin)* **1968**, *4*, 83.
- (15) Perkins, P. G.; Marwaha, A. K.; Stewart, J. J. P. *Theor. Chim. Acta* **1981**, *59*, 569.
- (16) Yanase, A.; Hasegawa, A. *J. Phys. C* **1980**, *13*, 1989.
- (17) Domashevskaya, E. P.; Terekhov, V. A.; Ugai, Ja. A.; Nefedov, V. I.; Serqushin, N. P.; Firsov, M. N. *J. Electron Spectrosc. Relat. Phenom.* **1979**, *16*, 441.
- (18) Kakizaki, A.; Sugawara, H.; Nagakura, I.; Ishii, T. *J. Phys. Soc. Jpn.* **1980**, *49*, 2183.
- (19) Myers, C. E. *High Temp. Sci.* **1974**, *6*, 309.
- (20) Myers, C. E.; Jung, E. D.; Patterson, E. L. *Inorg. Chem.* **1980**, *19*, 532.

* To whom correspondence should be addressed at the State University of New York at Binghamton.

† Visiting Professor, Ames Laboratory, Spring 1977 and Summer 1978.

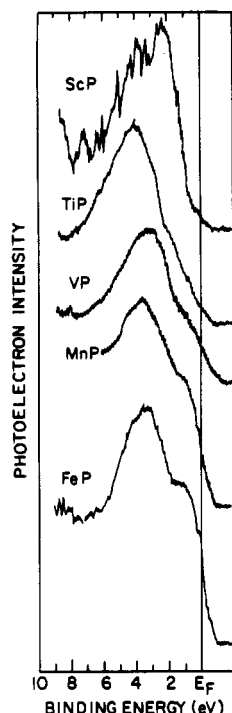


Figure 1. Photoelectron spectra of several first-row transition-metal monophosphides in the valence and conduction band region.

while side peaks (presumably from surface oxides) were observed to diminish during etching. This procedure generally reduced the principal impurity peak heights (O 1s and C 1s) to less than 10% of the metal $2p_{3/2}$ peak heights. Measurements were made with unmonochromatized Mg $K\alpha$ or Al $K\alpha$ radiation. The data were collected by signal averaging over the core level and the valence and conduction band regions. The spectrometer was calibrated with use of the procedures described by Powell and co-workers.²¹ The fit resulted in a work function for the instrument that is statistically uncertain by about 0.1 eV. No corrections were made for lattice site potentials, in keeping with conclusions described elsewhere.²² In order to assess whether the samples were sufficiently good conductors to preclude charging effects, test spectra were taken during the operation of an electron flood-gun. No shifts were observed in this procedure, and hence charging effects were presumed to be absent.

Results and Discussion

The valence and conduction band photoelectron spectra of the monophosphides are shown in Figure 1. These spectra are interpreted as being characteristic of the bulk material. It has been established²³⁻²⁵ for metals that bulk band structures can be determined accurately by angle-resolved ultraviolet photoelectron spectroscopy even though the electrons in this case are generated within a few angstroms of the surface. Inasmuch as the mean free path of photoelectrons in solids increases significantly with increasing electron energy,²⁶⁻²⁸ photoelectrons generated by X-rays, mutatis mutandis, are even more appropriately treated as arising from the bulk material. Additional support for the view that the electronic structure of a metal closely resembles the bulk within one or two atomic layers of the surface is provided by a recent theoretical study of interfaces.²⁹ The results for TiP, MnP, and

Table II. Metal $2p_{3/2}$ Binding Energies (eV)

	M	MP	M	MP
Sc	398.3	399.4	Mn	638.9
Ti	454.3	454.8	Fe	706.9
V	512.6	512.6		707.1

Table III. Phosphorus $2p_{3/2}$ Binding Energies (eV)

		VP	
P	129.9		129.1
ScP	127.7 ₅	MnP	129.4
TiP	128.4	FeP	129.5

FeP show features similar to those reported in the literature, including a low photoelectron intensity near the Fermi energy for TiP¹⁷ and shoulders on the valence band peak near the Fermi energy for FeP¹⁷ and MnP.¹⁸ In the last instance, the present X-ray photoelectron results most closely resemble the ultraviolet (synchrotron radiation) photoelectron spectrum¹⁸ for 130 eV photons. In ScP there is little photoelectron intensity at the Fermi energy, which indicates, by comparison with VS,³⁰ for example, that there is little Sc metal-metal interaction in ScP. This conclusion is consistent with the view⁶⁻⁹ of ScP as being weakly metallic; the low signal at the Fermi energy is consistent with a corresponding minimum in the calculated density of states.⁹ The conduction band spectrum of TiP, on the other hand, indicates a greater degree of metal-metal interaction but the photoelectron intensity at the Fermi energy is still not as pronounced as in VS.³⁰ It is therefore suggested that TiP is pivotal among the first-row monophosphides with a weakly metallic behavior intermediate between ScP and VP and later monophosphides which yield substantial photoelectron intensity in the vicinity of the Fermi energy, which indicates a marked metallic character. This pivotal, weakly metallic behavior of TiP is consistent with its unusual structure, which is intermediate between the NaCl-type structure characteristic of many nonmetallic solids, and the NiAs type, which is formed with one known exception (MnTe) only by metallic solids. The observed conduction band spectra thus suggest a regular progression with increasing d-orbital availability from the nominally saturated valence compound (groups IIIB-V, group 3 with group 15³⁵), ScP, to increasingly metallic monophosphides with metallic character being enhanced by increased metal d-orbital interactions. This view is consistent with the interpretation provided by Domashevskaya and co-workers¹⁷ for the results of their study of the X-ray spectra of TiP, CrP, MnP, FeP, and NiP. They concluded that the interaction of metal 3d and phosphorus 3s,p orbitals increased the density of d states near the Fermi energy. This interpretation is also supported by the results of an extreme UV study of the photoelectron spectrum of MnP using synchrotron radiation.¹⁸ Furthermore, recent calculations on MnP¹⁶ and other monophosphides including MnP^{6-9,15} support this view in showing an increasing density of states near the Fermi energy with an increasing number of metal d electrons.

With use of published cross sections,³¹ it is possible to estimate relative d-band/p-band intensity ratios under the assumption that three electrons are transferred from M(3d) to P(3p): ScP, 0; TiP, 0.05; VP, 0.34; MnP, 2.23; FeP, 3.63. While this trend is at least qualitatively followed by the spectra (uncorrected for scattered electrons), we conclude that this approach is inappropriate because of M(3d)-P(3p) overlap as evidenced by our core-level data and recent band theory results.⁶

The trend toward increased metallic character with increasing numbers of metal d electrons is reflected in the observed core-level binding energies, which are summarized in Tables II and III. The trend in phosphorus $2p_{3/2}$ energies parallels that reported by Domashevskaya and co-workers,¹⁷ but there is a consistent difference of over 5 eV. They report only energies for "2p" levels, and it is not apparent whether they used the value for spin $3/2$, spin $1/2$, or some average of the two. The splitting of 0.99 eV³²

(21) Powell, C. J.; Erickson, N. E.; Madey, T. E. *1979*, *17*, 361.

(22) Franzen, H. F.; Merrick, J.; Umaña, M.; Khan, A. S.; Peterson, D. T.; McCreary, J. R.; Thorn, R. J. *J. Electron Spectrosc. Relat. Phenom.* **1977**, *11*, 439.

(23) Inglesfield, J. E.; Holland, B. W. In "The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis"; King, D. A., Woodruff, D. P., Eds.; Elsevier: Amsterdam, 1981; Vol. 1, pp 233ff.

(24) Knapp, J. A.; Himpel, F. J.; Eastman, D. E. *Phys. Rev. B: Condens. Matter* **1979**, *19*, 4952.

(25) Thiry, P.; Choudery, D.; Lecante, J.; Guillot, C.; Pinchaux, R.; Petroff, Y. *Phys. Rev. Lett.* **1972**, *43*, 82.

(26) Steinhardt, R. G.; Hudis, J.; Perlman, M. L. *Phys. Rev. B: Solid State* **1972**, *5*, 1016.

(27) Battye, F. L.; Liesegang, J.; Leckey, R. C. G.; Jenkin, J. G. *Phys. Lett. A* **1974**, *49A*, 155.

(28) Battye, F. L.; Liesegang, J.; Leckey, R. C. G.; Jenkin, J. G. *Phys. Rev. B: Solid State* **1976**, *13*, 2646.

(29) Davenport, J. W.; Weinert, M. *Surf. Sci.* **1982**, *144*, 220.

(30) Franzen, H. F.; Sawatzky, G. A. *J. Solid State Chem.* **1975**, *15*, 229.

(31) Scofield, J. H. *J. Electron Spectrosc. Relat. Phenom.* **1976**, *8*, 129.

is too small to account for the discrepancy. Their metal "2p" levels are likewise displaced by about the same amount from the values reported here. It is probable that these differences reflect a significant calibration error in the results of Domhshevskaya and co-workers¹⁷ since the data reported in the present study are in reasonably good agreement with data obtained by others^{32,33} for the elements and for similar compounds. The $2p_{3/2}$ binding energies of metal and phosphorus show a maximum shift from the positions for the respective elements in the case of ScP, with a regular decrease in the shifts as the number of metal d electrons increases. The shifts in phosphorus peaks are greater and decrease more gradually than do the shifts in the metal peaks, presumably because of better shielding of the metal atoms by the conduction electrons. The trends are interpreted as evidence for decreasing ionicity, which is consistent with trends in the conduction band spectra and with the changes in crystal structure through the series of monophosphides. These observations are also consistent with shifts observed in related sulfides,³⁴ which were interpreted to mean that the occurrence of metallic interactions to form a d band

diminishes the tendency toward ionicity in the metal-nonmetal interactions, and this results, for the sulfides, in almost neutral (i.e., with negligibly shifted core levels) atomic species in the solid.

In addition to these trends within the phosphide series, there are important differences between the phosphides and the corresponding sulfides. Whereas ScP, a nominally saturated valence compound, is somewhat ionic, ScS is metallic with no net scandium to sulfur electron transfer.²² On the other hand, MnS is rather ionic,³⁴ but there is little net electron transfer in MnP. In the former example, both ScP and ScS have the NaCl-type structure,¹⁴ but in ScS there are more than enough electrons to fill the valence band, and there is significant electron delocalization. MnS has the NaCl-type structure, and its ionic nature is attributable to the electrons in the half-filled d shell not being available to form a conduction band. In contrast, MnP has one less electron per nonmetal atom, and its structure is a distortion of the NiAs-type structure, which affords significant metal-metal bonding.

Acknowledgment. The authors wish to thank Elizabeth L. Patterson for preparation of some of the samples used in this study and for assistance in making the measurements and Thuy-Hoa Nguyen for helpful discussions. This research was supported by the Office of Basic Energy Sciences, Materials Science Division, of the U.S. Department of Energy under Contracts W-7405-Eng-82 at Iowa State University and DEAC02-78ER04948 at the State University of New York at Binghamton. Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under the above contract. Partial travel support was provided by the Research Foundation of the State University of New York.

Registry No. ScP, 12202-43-6; TiP, 12037-65-9; VP, 12066-53-4; MnP, 12032-78-9; FeP, 26508-33-8.

- (32) Carlson, T. A. "Photoelectron and Auger Spectroscopy"; Plenum Press: New York, 1975; p 346.
 (33) Kowalczyk, S. P. Ph.D. Thesis, University of California, Berkeley, CA, 1976.
 (34) Franzen, H. F.; Umaña, M. X.; McCreary, J. R.; Thorn, R. J. *J. Solid State Chem.* **1976**, *18*, 363.
 (35) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III \rightarrow 3 and 13.)

Contribution from the Laboratoire de Chimie des Solides, Université de Nantes, L.A. au CNRS 279, 44072 Nantes Cedex, France

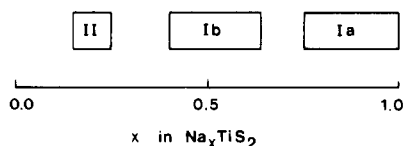
Effects of Sodium Intercalation in TiS_2 on the Electronic Structure of a TiS_2 Slab

M.-H. WHANGBO,*† J. ROUXEL,* and L. TRICHET

Received October 26, 1984

The band electronic structure of a TiS_2 slab was calculated as a function of the slab thickness by employing the tight-binding method. Flattening of a TiS_2 slab beyond a certain critical value is found to increase not only the density of states at the Fermi level for Na_xTiS_2 but also the anisotropy of electron distribution around Ti^{4+} . This explains why there occurs an abrupt increase in both the isotropic and anisotropic parts of the ^{23}Na Knight shifts in Na_xTiS_2 upon the Ib \rightarrow Ia phase transition.

Alkali-metal intercalation in layered transition-metal dichalcogenides has been the subject of numerous studies.¹ Sodium intercalation in TiS_2 has been found to give several distinct Na_xTiS_2 phases.² Accurate boundaries of these phases are difficult to ascertain, but all studies² reveal the presence of three single phases in the concentration range $0.15 < x \leq 1$. The phase boundaries determined recently by Molinie et al.^{2b} from X-ray measurements are shown in 1, where the II, Ib, and Ia phases span the concentration ranges $0.15 < x < 0.25$, $0.40 < x < 0.64$, and $0.75 < x \leq 1$, respectively. Phase II is a second-stage compound while the other two are first-stage compounds.



Structures of Na_xTiS_2 are often characterized by the crystal a and c parameters, where the c axis is perpendicular to a TiS_2 slab. As shown in 2 each Ti^{4+} ion is octahedrally coordinated, where the a parameter (i.e., the repeat distance within a TiS_2 slab) coincides with the length of a side of S_3^{6-} triangle. In 2 and 3 the thickness of a TiS_2 slab is denoted by d_1 , and the interlayer separation between adjacent TiS_2 slabs by d_2 . Thus the c parameter (i.e., the repeat distance along the c axis) is given by d

- (1) For leading references, see the following review articles: (a) Rouxel, J. "Physics and Chemistry of Materials with Layered Structures: Intercalated Layered Materials"; Lévy, F., Ed; Reidel: Dordrecht, 1979; pp 201-250. (b) Whittingham, M. S. *Prog. Solid State Chem.* **1978**, *12*, 41. (c) Bronger, W. "Physics and Chemistry of Materials with Layered Structures: Crystallography and Crystal Chemistry of Materials with Layered Structures"; Lévy, F., Ed.; Reidel: Dordrecht, 1976; pp 93-125.
 (2) (a) Rüdorf, W. *Chimica* **1965**, *19*, 489. (b) Leblanc, A.; Danot, M.; Trichet, L.; Rouxel, J. *Mater. Res. Bull.* **1974**, *9*, 191. (c) Silbernagel, B. G.; Whittingham, M. S. *Mater. Res. Bull.* **1976**, *11*, 29. (d) Winn, D. A.; Schemilt, J. M.; Steele, B. C. H. *Mater. Res. Bull.* **1976**, *11*, 559. (e) Hibma, T. *J. Solid State Chem.* **1980**, *34*, 97. (f) Nagelberg, A. S.; Worrel, W. L. *J. Solid State Chem.* **1979**, *29*, 345. (g) Zanini, M.; Shaw, J. L.; Tennenhouse, G. J. *Solid State Ionics* **1981**, *5*, 371. (h) Molinie, P.; Trichet, L.; Rouxel, J.; Berthier, C.; Charbre, Y.; Segran-san, P. *J. Phys. Chem. Solids* **1984**, *45*, 105.

* Camille and Henry Dreyfus Teacher-Scholar (1980-1985). Permanent address: Department of Chemistry, Box 8204, North Carolina State University, Raleigh, NC 27695-8204.