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The X-Ray Photoelectron Spectra of MnS, MnSe, and MnTe

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The core level binding energies and valence band spectra of MnS, MnSe, and MnTe have been examined by X-ray photoelectron spectroscopy. The results demonstrate that the compounds are substantially more ionic in character than related transition metal compounds, and that the compounds lack significant metal–metal interactions, accounting for the nontypical nature of the compounds as transition metal chalcides.

Introduction

For many years chemical bonding in compounds with the NiAs-type structure has been of interest principally because of the variety of magnetic and electrical properties of compounds which crystallize with this structure type, and because of the possibility of relating these properties to the behavior of the *d*-type electrons characteristic of metals which form binary compounds with this structure.

It was first realized a number of years ago that MnTe is a particularly interesting example of a compound which crystallizes with the NiAs-type structure (*1*). A great many of the solids which crystallize in the NiAs-type structure (e.g., TiS, $VS_{1.06+x}$, VP, FeS, CoS, etc.) and the related MnP-type (TiSe, $VS_{1.06-x}$, CrP, MnP, etc.) are metallic conductors and exhibit magnetic moments on the metal atoms which are indicative of extensive *d*-orbital involvement in the valence and conduction bands. On the other hand the magnetic susceptibility of MnTe suggests that the *d*-orbitals are largely nonbonding (*1*) (the effective moment has been reported to be 6.1 (*2*) and 5.1 (*3*) Bohr magnetons) and that the valence band of MnTe is formed principally from Mn and Te *p*-type orbitals. The rather long Mn–Mn distances in the solid (3.55 Å along *c* and 4.15 Å in the *a–b* plane (*4*)) support this view. Furthermore MnTe has been found to be a semiconductor above its Nèel temperature (*3*).

The bonding schemes proposed for MnTe (*1*, *5*) which have been based upon the rather indirect evidence of bond distances, magnetic susceptibilities, electrical resistivities, and cohesive energies can now be examined using the more direct information obtainable utilizing photoelectron spectroscopy. This information is of two complementary kinds, namely, core level shifts which are indicative of relative ionicity and covalency and the relative photoelectron intensities in the valence and conduction band regions which provide bases for comparisons of densities of states for bonding and conduction electrons. It was the purpose of the work undertaken here to examine the photoelectron spectrum of MnTe and, for purposes of comparison, of Mn, MnS, and MnSe as well in order to provide information relevant to the nature of bonding in these solids.

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Experimental Details

The samples were prepared from the elements in sealed, outgassed, and evacuated fused silica tubes. The samples were annealed at 500–700°C for 2 weeks. In the MnSe and MnTe cases the samples were then annealed in a tungsten container in high vacuum at 1100°C for about 4 h. The samples were handled in a N_2 filled glove box.

The products were characterized by Guinier X-ray diffraction. MnS and MnSe exhibited only diffraction lines characteristic of the NaCl-type structure with lattice parameters 5.221 Å (literature value 5.222 Å (*4*)) for MnS and 5.450 Å (literature value 5.45 Å (*4*)) for MnSe. MnTe exhibited only diffraction lines characteristic of the NiAs-type structure with a = 4.164 Å and c = 6.726 Å (literature values: a = 4.148 Å and c = 6.710 Å (*4*)).

The samples were crushed in a He atmosphere glove box with less than 1 ppm O_2 and 0.5 ppm H_2O and introduced from this atmosphere into an AEI ESCA 200 B photoelectron spectrometer. The data were collected by signal averaging over the core level and the valence and conduction band regions. Unmonochromatized AlK_α radiation was used with the narrowest entrance and exit slits available on the spectrometer (for Ag $3d_{5/2}$ fWHM = 1.0 eV). The samples were pressed onto In foil and were etched by argon ion bombardment (5-kV ions for about 1 hr) until impurity peak heights in the full scan spectra (i.e., the O and C 1s peaks) were less than 10% of the Mn $2P_{3/2}$ peak heights.

The spectrometer was calibrated against the absolute calibration binding energy values (*6*): 368.0 eV (Ag $3d_{5/2}$), 84.0 eV (Au $4f_{7/2}$), 335.5 eV (Pd $3d_{5/2}$), 71.3 eV (Pt $4f_{7/2}$), and the Fermi edge in Pd by means of a least squares fit of the relativistic calibration equation (*6*):

$$E_e - E_m = -CE_m + (E_m^2/2E_0)$$

where E_e is the electron-energy, E_m is the measured kinetic energy, C is an instrumental calibration constant, and E_0 is the rest mass energy of the electron. The fit resulted in a work function for the instrument that is statistically uncertain by less than 0.1 eV.

TABLE I

Mn $2P_{3/2}$ BINDING ENERGIES (RELATIVE TO ABSOLUTE B.E.'S OF REF.(*7*))

Cpd	Binding energy (eV ± 0.2)
Mn	638.4
MnS	640.8
MnSe	640.2
MnTe	640.7
MnP	638.3[a]

[a] C. E. Myers and H. F. Franzen, unpublished results.

The binding energies reported here were not corrected for lattice site potentials. The lattice site potentials calculated on the basis of the point charge model have been shown to greatly overestimate the contributions of lattice site potentials to the observed shift in the alkaline earth chalcides (*7*). Since the compounds under consideration in this work are, if anything, less ionic than the alkaline earth chalcides this contribution is considered here to be negligible.

TABLE II

NONMETAL BINDING ENERGIES

Cpd of the nonmental	Level	Binding energy
CaS	$2P_{3/2}$	161.0[a]
MnS		160.8
TiS		162.3[a]
Se	$3P_{3/2}$	160.9[a]
MnSe		160.0
CaSe		159.1[a]
MnTe	$3d_{5/2}$	572.5
Te		573.1[b]
TeO_2		576.1[b]
TeO_3		577.3[b]
MnP	$2P_{3/2}$	128.8[c]
P		129.0[c]

[a] Ref. (*8*).
[b] Ref. (*9*).
[c] C. E. Myers and H. F. Franzen, unpublished results.

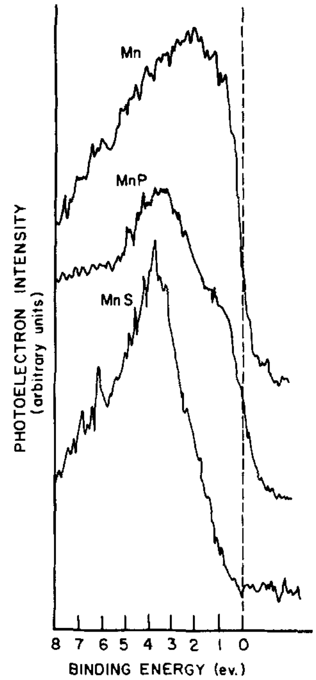

FIG. 1. Valence and conduction band X-ray photoelectron spectra of Mn, MnP, and MnS.

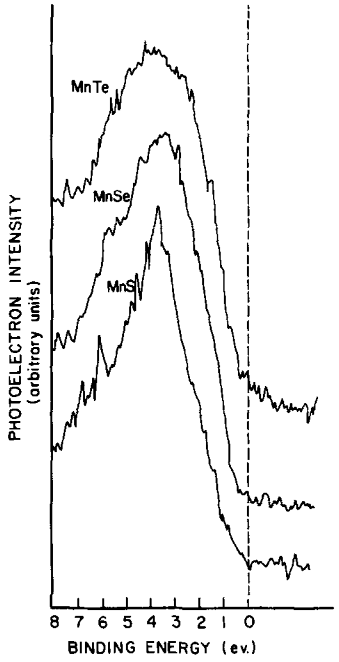

FIG. 2. Valence band X-ray photoelectron spectra of manganese monochalcides.

Results

The Mn $2P_{3/2}$ core level binding energies obtained in the three monochalcides are listed, along with the binding energies observed for Mn in MnP and the pure metal, in Table I. The binding energies of the nonmetal elements are listed in Table II together with some values obtained in recent work by this group and with some values from the recent literature. The binding energies obtained for Mn and S in MnS here are in excellent agreement with values obtained in previous work (*8*) using a different instrument. The photoelectron spectra in the valence regions are shown in Figs. 1 and 2.

Discussion

The data of Table I demonstrate that there is a fundamental difference between the three chalcides and MnP. This difference is that Mn in the chalcides is substantially more cationic in character than Mn in MnP. A comparison of the Mn binding energies in Mn and MnP indicates that Mn in MnP is very nearly neutral.

The substantial ionicity of Mn in MnS was also previously noted in a comparison of S $2P_{3/2}$ binding energies for the early first-row transition metal monosulfides (*8*) (cf. the first three entries of Table II). The other binding energies of Table II corroborate this conclusion. For example, the Se–MnSe–CaSe comparison indicates that MnSe is intermediate in ionicity between neutral Se and strongly ionic CaSe, the tellurium compound binding energies (*9*) indicate an anionic character for Te in MnTe and the MnP–P comparison confirms the neutral, covalent nature of MnP.

Thus, in comparison with other transition metal monosulfides and MnP, the manganese monochalcides appear to be significantly ionic in character. The comparison of spectra in Fig. 1 provides insight into the origin of this difference. The MnP valence-conduction band spectrum clearly shows a peak at a binding energy of 1 eV and a significant intensity at the Fermi energy. The states giving rise to this intensity are generally attributed to a metallic *d*-band. In fact, the principal features of the MnP spectrum can be seen to be roughly equivalent to a superposition of the MnS and Mn spectra if the (arbitrary) peak heights are appropriately adjusted. Such a peak in the neighborhood of the Fermi energy is characteristic of compounds thought to have *d* bands arising from metal–metal interactions (e.g., VS (*10*)), and thus the absence of such a peak in the spectrum of MnS is indicative of the absence of significant Mn–Mn interactions. Thus the spectrum is in good accord with the semiconducting behavior and rather long Mn–Mn distances (≥ 3.69 Å) of this solid.

The comparison of Fig. 2 then indicates that this *d*-band is similarly missing in both MnSe (with the NaCl-type structure) and MnTe (with the NiAs-type structure), and thus that the principal feature of the bonding model proposed in 1957 by Pearson (*1*), namely, the nonbonding character of the Mn 3*d* electrons, is indeed correct. Furthermore the increasing width of the valence band spectra in the series MnS–MnSe–MnTe suggests, in agreement with the generally accepted view, that the bonding becomes increasingly more delocalized with increasing atomic number of the chalcogen.

Conclusion

The principal conclusion of this work is that the bonding model proposed for MnTe in (*1*) is consistent with the photoelectron spectrum. The significance of this model is that it provides a case in which metallic conductivity (MnTe is metallic below its Néel temperature) in a NiAs-type solid does not arise from metal–metal interactions. Thus the model suggests that there can be contributions to the delocalization of electrons that have their origin in metal–nonmetal interactions, indicating a variable and thus potentially useful character to the nonmetal bonding in the case of Te at least and perhaps for Se and S as well.

Finally, it can also be concluded that metal–metal bonding is not required for the formation of the NiAs-type structure although the bulk of the structural and physical property information would suggest that metal–metal interactions do serve to stabilize the structure.

Acknowledgments

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