

X-ray photoemission studies of the valence bands of nine IV-VI compounds*R. B. Shalvoy,[†] G. B. Fisher,[‡] and P. J. Stiles*Department of Physics, Brown University, Providence, Rhode Island 02912*

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Valence-band spectra have been obtained by means of x-ray photoemission spectroscopy for the group IV-VI compounds GeS, GeSe, GeTe, SnS, SnSe, SnTe, PbS, PbSe, and PbTe. These spectra, taken under ultrahigh-vacuum conditions with unmonochromatized Mg x rays, are presented and discussed in terms of previously reported valence-band spectra and band-structure calculations. It is observed that the valence bands of the orthorhombic structured compounds (GeS, GeSe, SnS, and SnSe) which have not been previously reported and for which no band-structure calculations have been published are closely related to those of the NaCl-structured compounds despite the two-dimensional character of the orthorhombic structure.

I. INTRODUCTION

The IV-VI compounds (group-IV cation, group VI anion) display a variety of properties that have attracted considerable attention^{1,2} to some structurally simple (NaCl) members of the family, the lead chalcogenides and SnTe. However, relatively little is known about the orthorhombic structured members of this family (GeS, GeSe, SnS, and SnSe). Recently attention has been drawn to GeS,³⁻⁵ which has a structure that displays both two- and three-dimensional character.⁶ A definite anisotropy has been observed for some of its optical properties.^{3,5}

The orthorhombic structure may be viewed as a small distortion of the NaCl structure with the expectation that the properties of the orthorhombic structured materials will behave in a similar fashion to those of the NaCl-structured materials. This behavior has been observed for some bond-related properties.⁷⁻⁹

The band structures of the cubic IV-VI compounds are well known¹⁰⁻¹² and have been very useful in understanding the properties of these materials.^{1,13} However, to date a more complete understanding of the relation between the orthorhombic and NaCl-structured compounds has been limited as there are no band-structure calculations for the orthorhombic IV-VI compounds.

It is well known that the x-ray-photoemission (XPS) valence-band spectrum, sometimes called the photoemission density of states (PDOS) is closely related to the initial (valence-band) density of states.^{13,14} Good agreement between the PDOS and theoretically calculated densities of states^{13,15-18} has been observed for those IV-VI compounds for which band structures have been calculated. This property of the XPS PDOS will be used to extend our understanding of the band structure of IV-VI compounds to the orthorhombic-

structured compounds.

The XPS measurements were performed on an AEI ES200A electron spectrometer using unmonochromatized Mg radiation and having a source chamber vacuum of 1×10^{-9} Torr during the data collection. The system resolution is approximately 0.9 eV, limited by the x-ray linewidth. Samples were polycrystalline except for GeS, SnS, and SnSe which were single crystals. Cleaning was performed in a dry nitrogen filled Glove Bag attached to the spectrometer entrance valve immediately prior to insertion into the spectrometer by cleaving the single crystals with Scotch tape or by scraping the other sample surfaces with a razor blade. This pretreatment was very effective as only weak carbon and oxygen impurity peaks were observed, ensuring that the valence spectra obtained were due solely to the bulk sample material. GeTe and SnTe did require brief (30 sec, 500 eV) argon-ion etching to remove some surface contaminants. Minimal contaminant buildup was subsequently observed.

The major limitation of the experiment was the impinging of the $K\alpha_{3,4}$ satellite radiation peak for the nearby cation core d level on the weaker valence-band levels. While this is no problem for the germanium compounds for which the core d level is deep enough (30 eV) so that the satellite peak occurs outside the valence-level region (about 20 eV), the satellite peak obscures part of the valence levels in the tin compounds, and more in the lead compounds. The consequences of this will be discussed below.

II. RESULTS

The valence-band spectra are shown in Fig. 1. The peak energies are listed in Table I and have been corrected for charging. The energies are referred to the spectrometer Fermi level. As the data obtained did not provide information on the

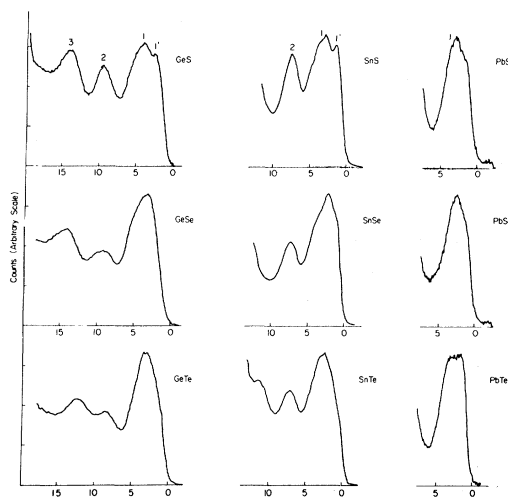


FIG. 1. Experimentally determined valence-band spectra taken with unmonochromatized Mg radiation. All energies are referred to the Fermi level of the spectrometer. Peaks 1 and 1' are due to the bonding p electrons, and peaks 2 and 3 are due to the cation and anion s electrons, respectively.

deeper bands in the lead compounds, spectra taken with monochromatized radiation¹³ are reproduced in Fig. 2.

The valence bands occurred in a three peaked structure for all materials. The lower-most peaks have been attributed to the anion and cation s states although the cation s states show evidence of some hybridization with the bonding p electrons.^{13,19} These peaks, labeled 3 and 2, respectively, in keeping with the established notation, display no structure and are as narrow as the deeper core s levels.⁹ The upper-most peak labeled 1 has been attributed to the bonding p electrons and displays some structure, notably peak 1'.

Our results are in good agreement with those previously reported.^{13,14,16,17} As the anion s peak in SnTe is not fully resolved from the satellite d peak, its width has been estimated from the spectrum given in Ref. 16. The spectra for SnS and SnSe are shown without peak 3 as that peak is obscured by a satellite peak; however, as there are currently no other studies of these compounds, the incomplete spectra are shown.

III. DISCUSSION

The most striking feature of the valence-band spectra in Figs. 1 and 2 is the overall similarity of the spectra. This similarity has been observed in the reflectance spectra²⁰ and stems from the isoelectronic and approximately isomorphous nature of the IV-VI compounds. The peaks have been

identified from the band structure¹³ and charge density calculations.¹⁹ The clear separation of peak 3 from the remainder of the valence bands shows the corelike nature of the level which is reflected in the flatness of the band in the band structure.¹⁹ Peak 2 contains some p states as well as the cation s states.^{15,19} The p -derived bands (1 and 1') show appreciable structure and contain the bulk of the information on the bonding.

SnTe and GeTe have the largest nonstoichiometries ($\sim 10^{21}$ cation vacancies/cm³)²¹ of all the IV-VI compounds and consequently, the Burstein shift²² of the Fermi level towards the valence bands should be the largest for these compounds.

TABLE I. Binding energies and full width at half maximum (FWHM) of the peaks observed in the valence-band spectra. All energies are given in eV and are referred to the Fermi level of the spectrometer. The separation of the cation and anion s states (peaks 2 and 3, respectively) is listed for those compounds in which both peaks were unobscured by the satellite peak due to the nearby cation d level.

	Peak	Binding energy	FWHM	$\Delta E(2-3)$
GeS	1'	2.2		
	1	3.7	5.0	
	2	9.3	3.3	
	3	13.8	3.1	4.5
GeSe	1	3.1	4.3	
	2	8.8	3.4	
	3	14.1	3.0	5.3
GeTe	1	3.0	4.2	
	2	8.2	4.2	
	3	12.0	3.9	3.8
SnS	1'	1.5		
	1	2.9	5.0	
	2	7.4	2.4	
SnSe	1'	1.0		
	1	2.3	5.0	
	2	7.3	2.4	
SnTe	1	2.7	4.4	
	2	7.2	2.6	
	3	11.6	2.6 ^a	4.4
PbS ^b	1'	1.4		
	1	2.7	3.7	
	2	8.4	1.5	
PbSe ^b	1'	1.4		
	1	2.6	3.4	
	2	8.6	1.8	
PbTe ^b	1	2.3	3.8	
	2	8.2	2.3	
	3	11.7	2.5	3.5

^a Estimated from spectrum in P. C. Kemeny and M. Cardona, *J. Phys. C* **9**, 1361 (1976).

^b Results for peaks 2 and 3 of the lead compounds are reproduced from F. R. McFeely, S. P. Kowalczyk, L. Ley, R. A. Pollak, and D. A. Shirley, *Phys. Rev. B* **7**, 5228 (1973).

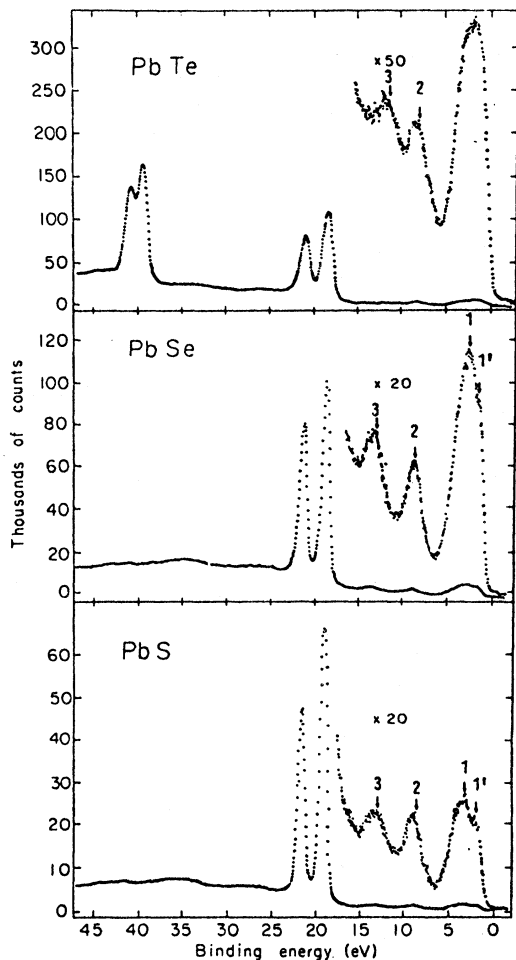


FIG. 2. Experimental valence-band spectra and nearby core levels of the lead compounds taken with monochromatized Al radiation as shown in Ref. 13.

This effect is clearly seen in Fig. 1 as the Fermi level is near to the top of the valence bands for SnTe and GeTe, although the exact position is obscured by the limited resolution of the system.

Peak 1' is the most striking feature of the p bands. It is resolved in GeS and SnS and appears as an edge in SnSe, PbSe, and PbS. It most likely would have been observed in the GeSe spectrum as well if a single-crystal sample had been available. This structure is attributed to anion p states in part through the work of Fisher *et al.* on the $\text{Ge}_x\text{Te}_{1-x}$ alloys²³ and in part through an accidental observation. It was observed that following an extended sputtering of a GeS sample the intensity of the sulfur peaks had decreased relative to the germanium peaks (due to preferential sputtering²³) and that peak 1' appeared only as an edge rather than a distinct peak (Fig. 3). It should be noted that polycrystalline samples of GeS showed only

an edge for peak 1'.

The valence-band spectra for the four orthorhombic structured IV-VI compounds are new results. Given the significant structural distortion of these materials from the NaCl structure prototypical of the other IV-VI compounds,⁹ a comparison of the PDOS for these compounds with those of the NaCl-structured compounds should provide information on the significance of this distortion on the band structure and the electronic properties.

Care is required in comparing spectra taken with unmonochromatized and monochromatized radiation (Figs. 1 and 2, respectively). Nonetheless the PDOS of the orthorhombic IV-VI compounds appear very similar to those of the cubic IV-VI compounds. The three peaked structure and the reduction of the 1, 1' splitting for the heavier materials are all observed for all material. As a consequence of this we conclude that the orthorhombic distortion is not a major influence on the density of states of these compounds. This suggests that the orthorhombic distortion might be treated as a small perturbation if the band structure of these compounds were to be calculated approximately as has been done for GeTe.¹⁵ This is further evidence of the overall similarity of the IV-VI compounds and provides justification for treating them as a unified family.

The separation of peaks 2 and 3 has been used as a measure of the ionicity of the bonding of a material.²⁴ This spacing has been observed²⁴ to depend on the crystal lattice parameters and the bond ionicity.^{25,26} The data reported here have been used to test the approach proposed. The

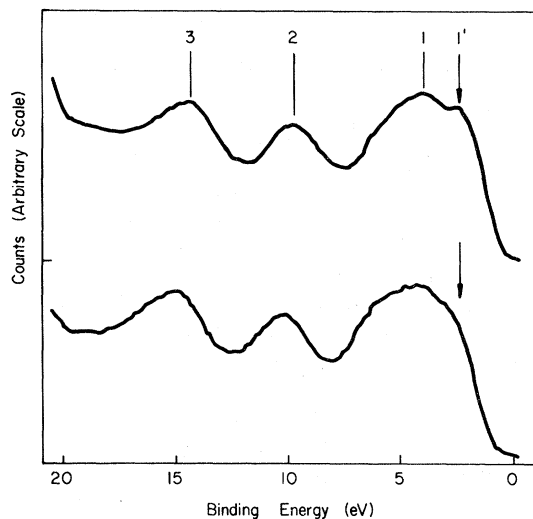


FIG. 3. The valence-band spectrum of single-crystal GeS before and after argon-ion sputtering. Peak 1' has been clearly weakened in intensity.

findings are discussed in more detail elsewhere,⁹ but we found that the specific approach used resulted in ionicities that disagreed with most other scales that have been calculated for these compounds. It does appear that there is some ionicity information in these data although it may be present in a more subtle form.^{25,26}

IV. CONCLUSIONS

We have obtained moderate resolution XPS valence-band spectra of nine IV-VI compounds. The spectra of the orthorhombic structured compounds show a strong similarity to those previously reported for the NaCl-structured compounds. We conclude that the band structure of the orthorhombic-structured compounds (which has not been calculated) may be expected to be closely related to

that of the NaCl-structured compounds. This suggests that the structural distortion of the orthorhombic structure from the NaCl structure may be able to be treated as a small perturbation to the density of states for the IV-VI compounds.

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