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Electronic structure of MPS$_4$ (M = In, Ga, Al, and B) compounds

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Tight-binding calculations of the electronic structure of the MPS$_4$ (M=B, Al, Ga, and In) thiophosphate family, are performed. The theoretical density of states (DOS) is compared with the x-ray photoemission spectroscopy valence-band spectrum for InPS$_4$, from which we are able to identify the main character of the experimental peaks. Differences in the density of states due to changes in the group-III element are also analyzed, since there are marked effects in the DOS due to the differences in the atomic radii of the M element. We predict these compounds to be insulators and from the calculated charges we are able to account for the oxidation number associated to each atom in these systems.

I. INTRODUCTION

Sulfur passivation of semiconductor surfaces is considered, in metal-insulator-semiconductor field-effect-transistor technology,[1,2] as an alternative passivation method to the oxidation of semiconductor surfaces. The InPS$_4$ thiophosphate is of interest because of its eventual presence in films formed after sulfur passivation of InP surfaces.[3] A similar situation can be expected in the GaP and AlP semiconductors due to the existence of well-established MPS$_4$ sulfides. It is worth characterizing both experimentally and theoretically the electronic structure of these materials and this paper is a contribution to its theoretical understanding. Some experimental characterization is available for the crystalline InPS$_4$ (Ref. 4) and GaPS$_4$ (Ref. 5) compounds but, to our knowledge, no theoretical analysis has been made on these systems.

In this work, we consider the electronic structure for the whole family of MPS$_4$ (M=In, Ga, Al, and B) compounds, where we have included the BPS$_4$ compound for completeness. A tight-binding (TB) method is used to obtain the total and partial density of states [(DOS) and (PDOS)]. The TB method applied here, even though nonself-consistent, was successfully employed to describe a variety of complex semiconductor oxides,[6–8] and in these cases, allow us to give a coherent description for the whole thiophosphate family. The method does not contain particular parametrizations emphasizing its predictive character when applied to systems where no experimental information is available. Our aim in this paper is to compare the calculated DOS with the valence band x-ray photoemission spectroscopy (XPS) spectrum for InPS$_4$, where we are able to recognize the atomic contributions to each experimental peak, and to predict these contributions to the DOS for the remaining compounds. Finally, we correlate the electronic structure with the chemical nature of the group-III element.

II. ATOMIC STRUCTURE DESCRIPTION

In Table I, some structural information and the average nearest-neighbors distances for all sulfides is presented. All of them are formed by tetrahedral units of PS$_4$ and MS$_4$ linked together by a common sulfur atom. In spite of their similar local environments, the crystalline tridimensional networks are very different. In BPS$_4$ (Ref. 12) parallel, noncoupled, chains of alternated tetrahedral complexes, sharing two common sulfur atoms, are present. In AlPS$_4$ (Ref. 11) one also found uncoupled chains of tetrahedral units, also connected by sharing a common edge of the tetrahedra, although in this case, the chains are perpendicularly oriented. In GaPS$_4$ (Ref. 10) these units are linked as to form uncoupled planes of tetrahedra causing a perfect cleavability parallel to (001) plane. Finally in InPS$_4$, we can recognize chains of tetrahedral sites growing along the [111] direction, all of them being bonded to the nearest parallel chains.

TABLE I. Average nearest-neighbors distances (in Å).

InPS$_4$^{a} Tetragonal-$I\bar{4}$		GaPS$_4$^{b} Monoclinic-$P2_1/c$		AlPS$_4$^{c} Orthorhombic-$P222$		BPS$_4$^{d} Orthorhombic-$I222$	
In-S	2.47	Ga-S	2.28	Al-S	2.1	B-S	1.89
P-S	2.53–2.04^e	P-S	2.05	P-S	2.1	P-S	2.16
In-P	3.60	Ga-P	2.89	Al-P	2.8	B-P	2.63
S-S^f	3.27	S-S	3.34	S-S	3.49	S-S	3.51
	3.57		3.70		3.49		3.08

[a] Reference 9.
[b] Reference 10.
[c] Reference 11.
[d] Reference 12.
[e] Reference 13.
[f] The first row corresponds to PS$_4$ tetrahedra and the second one to MS$_4$ tetrahedra.

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III. THEORETICAL MODEL

A minimal basis set including valence *s* and *p* atomic states were considered for each atom. The minimal basis is assumed, as it is usual in TB calculations, to form an orthonormal set. First nearest-neighbor interactions were considered and S-S second nearest-neighbor interactions between connected tetrahedral units were also included. For the nondiagonal matrix elements of the Hamiltonian, we have used the same general form employed in Refs. 6–8. This general parametrization takes into account the atomic radii of the component chemical species giving the possibility to have a variety of nearest-neighbor distances, as it is the case for the compounds under consideration and in the majority of semiconductor oxides.[6–8] A complete account of the theoretical method used here, can be found in Ref. 7. We have checked that eight special points[14] in the Brillouin zone are sufficient to calculate the DOS for all compounds in the family. The intra-atomic terms are taken from the Herman-Skillman atomic energies.[15] Similar to the case of semiconductor oxides,[6–8] a good agreement between the DOS and XPS spectrum as well as the gap value for $InPS_4$ is obtained by shifting upwards the phosphorus levels by 6 eV relative to the sulfur levels. Orthogonalization of the phosphorus to the sulfur states may account for such shifting due to the close distance between these atoms. Similar shifts were used for the remaining sulfides.

IV. RESULTS AND DISCUSSION

A. $InPS_4$

The XPS valence-band spectrum as well as the theoretical DOS for $InPS_4$ are shown in Fig. 1 and are compared with the DOS obtained for the other thiophosphates in this family. Table II collects the main contributions to each peak of Fig. 1. These are derived from the detailed analysis of PDOS given in Fig. 2. The top of the valence band has a sulfur 3*p* character for all compounds. Phosphorus states contribute to peaks *b* and *c* (P 3*p* and P3*s*, respectively). Peak *d* accounts for the sulfur-sulfur 3*s* interactions. We can observe in Fig. 2 another peak at the bottom of the valence band, also having a sulfur 3*s* character. This peak is not seen in the experimental XPS spectrum of Fig. 1. The reason being that, at this energy, the XPS spectrum has a peak of strong intensity corresponding to the indium 4*d* states (core level states in our calculations). A similar situation has been found in $In(PO_3)_3$ (Ref. 6) where the peak at the bottom of the valence band is completely hidden behind the very intense indium 4*d* XPS peak.

B. $GaPS_4$, $AlPS_4$, and BPS_4

As can be seen in Table II, the electronic structure of $GaPS_4$ is similar to that of $InPS_4$. For the other compounds in this family, we found differences in peaks *b* and *c* of Fig. 1. For the $AlPS_4$ case, peaks *b* and *c* collapse to a broad signal, although one can still distinguish the atomic contributions indicated in Table II. On the other hand, for BPS_4, peak *c* appears again, now as a shoulder of *b* at lower energies. The main character of peak *c* is given by the sulfur 3*p* and boron 2*s* states.

It is very interesting to analyze these results consider-

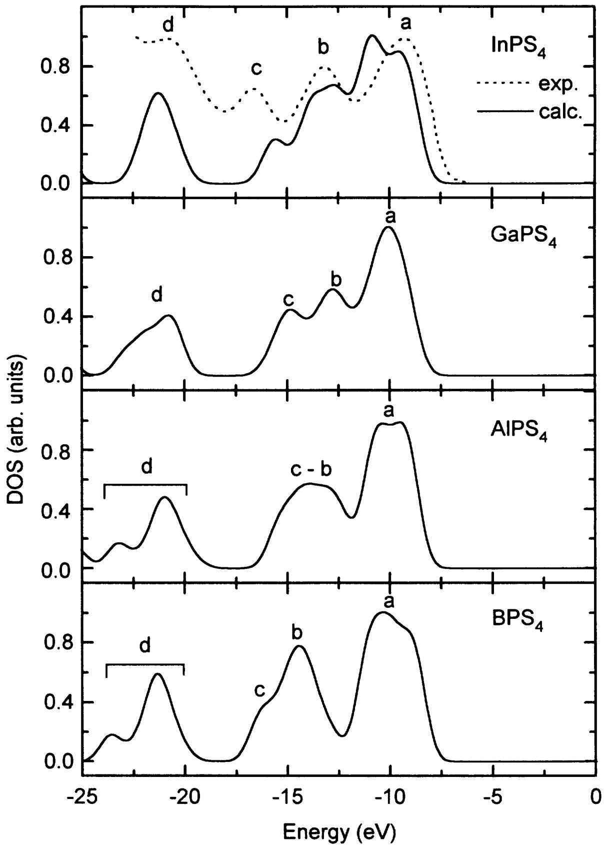

FIG. 1. Calculated total density of states (DOS) for the MPS_4 (M = In, Ga, Al, and B) family compounds. The experimental XPS valence-band spectrum for $InPS_4$, taken from Ref. 4, is also included for comparison (dashed line). All curves are in arbitrary units and have been normalized to their maximum value. The main contributions to the different peaks are collected in Table II. All DOS levels have been broadened by 0.5 eV wide Gaussians in order to compare with the XPS spectrum.

TABLE II. Main character for the peaks of Fig. 1.

Compound	Peak	Main contribution
$InPS_4$	*a*	S 3*p*
	b	S 3*p* and P 3*p*
	c	S 3*p* and P 3*s*
	d	S 3*s*
$GaPS_4$	*a*	S 3*p*
	b	S 3*p*, P 3*p*, and Ga 4*p*
	c	S 3*p* and P 3*s*
	d	S 3*s*
$AlPS_4$	*a*	S 3*p*
	b	S 3*p* and Al 3*p*
	c	S 3*p*, P 3*s*, and Al 3*s*
	d	S 3*s*
BPS_4	*a*	S 3*p*
	b	S 3*p* and B 2*p*
	c	S 3*p* and B 2*s*
	d	S 3*s*

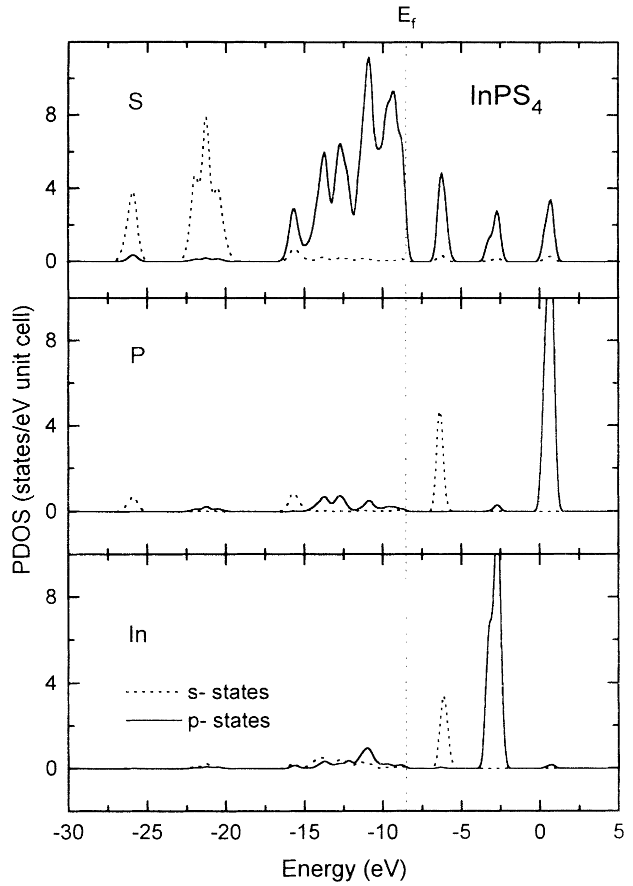

FIG. 2. Calculated partial density of states (PDOS) for $InPS_4$. Each level has been broadened by a 0.2 eV wide Gaussian in order to keep the PDOS structures.

ing the sequence In-Ga-Al-B, of group-III in the Periodic Table. All these atoms have the same number of valence electrons and, consequently, it is expected that all of them will be bonded to S in a similar form. Even if that is exactly what is found—all of them form MS_4 tetrahedral units—the crystalline structure are very different. In Table I, we can observe that the mean M-S distances decrease when going from In to B, due to the decreasing atomic radii. When this distance is compared, for each compound, with the corresponding P-S distance (nearly the same in all compounds[13]), we can extract two evidences that have observable effects in the DOS of Fig. 1. The first one is the change of the nature of peak *c*: typically a phosphorus 3*s* character in $InPS_4$ and a boron 2*s* character in BPS_4. This can be understood considering that in BPS_4 the shortest nearest-neighbor distance corresponds to boron-sulfur bonds and not to the phosphorus-sulfur bonds, as it is the case in the other compounds. The B-S interactions are then increased over the P-S interactions. For $AlPS_4$, the M-S and P-S distances are the same and Al as well as P states contribute to peaks *b* and *c* in Fig. 1. The second evidence from Table I is that the size of the tetrahedron MS_4 decreases when going from In to B, giving shorter S-S bond distances. This increases the sulfur-sulfur interactions and splits the single peak *d* of Fig. 1 into two for $AlPS_4$ and BPS_4.

Reference 16 gives the calculated values of the free-atom photoionization cross sections corresponding to the excitation energy of XPS experiments. Table III collects these values for the atoms in the thiophosphate family, normalized to the S 3*p* cross-section value. One can use these free-atom values as an approximation to the actual photoemission cross sections of these atoms when they are placed in different compounds. Thus, from the values of Table III, we predict that the states of boron in BPS_4 as well as the aluminum 2*p* states in $AlPS_4$ practically will not be present in their respective XPS valence-band spectrum. On the other hand, phosphorus 3*s* states and sulfur 3*s* will increase their intensity by factors of about 2.9 and 3.8 times, respectively, as compared to the sulfur 3*p* states. This allows one to understand the intensity of the peaks *c* and *d* in the $InPS_4$ XPS spectrum of Fig. 1.

In Ref. 5 measurements of the optical gap for single crystals of $InPS_4$ and $GaPS_4$ are reported. Their values are 3.2 eV ($InPS_4$) and 3.3 eV ($GaPS_4$), respectively. $AlPS_4$ and BPS_4 were found to be hygroscopic and values for the optical gap has not been measured. From our results, we conclude that the family of compounds under study are insulators, with decreasing gaps in the sequence: $InPS_4$-$AlPS_4$-$GaPS_4$-BPS_4. We predict that in all cases, the bottom of the conduction band is formed by phosphorus 3*s* states and sulfur 3*p* states.

Finally, in Table IV the nonself-consistent calculated atomic charges for all compounds are reported. The differences in the number of electrons for an atom placed in different environments are generally analyzed in terms of the oxidation number (N) concept. This is defined as the net charge (in units of e) that an atom would have if all electrons in each bond were assigned to the most electronegative atom. In Ref. 7, it was pointed out that n_s (the number of s electrons) is the driving parameter for the oxidation number (i.e., a lone-pair existence or not). From Table IV we observe that n_s, for all elements of group-III and phosphorus atoms are far below two, indicating that there are no lone pairs present being that all valence electrons are engaged in the bonds. Therefore, we conclude that all M atoms have an oxidation number $N_M = +3$ and the phosphorus atoms in all of these compounds have an oxidation number of $N_p = +5$. Similarly the oxidation number for sulfur is $N_S = -2$ along the whole family. Thus, from the calculated atomic charges, we obtain the usual oxidation number representation for this family: $M^{(3+)}P^{(5+)}(S^{2-})_4$. It is to be stressed that the oxidation number concept is an ionic representation

TABLE III. Calculated free-atom photoionization cross sections (per electron) at the excitation energy of XPS experiments (1486.6 eV), normalized to the S 3*p* cross-section value (adapted from Ref. 16).

	ns	*np*
B ($n=2$)	0.57	0.00
Al ($n=3$)	1.38	0.17
Ga ($n=4$)	2.28	0.92
In ($n=5$)	1.95	1.01
P ($n=3$)	2.88	0.63
S ($n=3$)	3.78	1.00

TABLE IV. Calculated atomic charges (in electrons) for the whole family of compounds. n_{at}: number of valence electrons in the isolated atom. S1, S2, etc. correspond to the S atoms crystallographically different.

Compound	Component	n_s	n_p	n_{total}	n_{at}
$InPS_4$	In	0.976	1.145	2.121	3
	P	0.752	1.226	1.978	5
	S	1.926	5.049	6.975	6
$GaPS_4$	Ga	0.989	1.370	2.359	3
	P	0.757	1.150	1.907	5
	S1	1.925	4.994	6.919	6
	S2	1.930	5.066	6.996	6
	S3	1.932	5.042	6.974	6
	S4	1.926	4.919	6.845	6
$AlPS_4$	Al	0.745	1.548	2.293	3
	P	0.889	1.001	1.890	5
	S1	1.929	5.012	6.941	6
	S2	1.932	5.036	6.968	6
BPS_4	B	0.867	2.262	3.129	3
	P	0.917	0.964	1.811	5
	S	1.918	4.829	6.747	6

and does not correspond to the actual charges involved.

The calculated charge transferred are in qualitative agreement with the values of the electronegativity for the elements, boron being a special case among the group-III elements. The atomic levels of boron are deeper in energy than in the other atoms of the same group. Besides the potential generated by the presence of sulfur atoms, the electrons on phosphorus feel an additional potential arising from the boron atoms. Then, the valence electrons of phosphorus are spread out on sulfur and boron. Thus, the net charge on boron is slightly above the atomic value. The same conclusion may be reached by considering that boron is the most electronegative (2.0) element of group III (1.5 for Al, Ga, and In atoms), when compared to the electronegativity value of P (2.1) and S (2.5) atoms.

V. CONCLUSIONS

We have performed band-structure calculations for the thiophosphate family MPS_4 (M=In, Ga, Al, and B) using the tight-binding method. We have been able to correlate the density of states with the chemical nature of group-III element present in each compound. In particular we have identified the atomic states contributing to the experimental valence-band XPS spectrum measured for $InPS_4$. We predict these compounds to be insulators and that sulfur 3*p* states form the top of the valence band in all compounds while its 3*p* and phosphorus 3*s* states gave the main character to the bottom of the conduction band. Differences in the atomic radii when going from In to B produce two observable features in the DOS: the peak *c* (Fig. 1) changes in nature (3*s* of phosphorus in $InPS_4$ and 2*s* of boron in BPS_4) and the splitting of peak *d* due the increasing sulfur 3*s*-sulfur 3*s* interactions in $AlPS_4$ and BPS_4. An analysis of the calculated charges allow us to conclude that P and S atoms have the same oxidation number in all compounds ($N_P=+5$ and $N_S=-2$, respectively), and also that the $N_M=+3$ for all atoms of group III. Finally, considering the free-atom photoionization cross sections (calculated at the excitation energy of XPS experiments) for the boron states in BPS_4 and the aluminum 2*p* states in $AlPS_4$, we predict that even if they are present in the calculated DOS, they would not be present in their respective XPS valence-band spectrum.

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[13] In Ref. 5, an $InPS_4$ single crystal was characterized by using x-ray crystallography. The P-S nearest-neighbor distance obtained is significantly smaller than that reported in Ref. 9 (2.53 Å). We assume that there might be a misprint in this reference. Interchange of *x* and *y* coordinates assigned to P, gives for the P-S nearest-neighbor distance practically the same value corresponding to those found in the other members of the family, as well as the same value for the P-S distance found in Ref. 5, leaving unchanged all other distances.

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