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Universal band structures for group-V elements and IV-VI compound semiconductors

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The tight-binding band structures of the group-V elements As, Sb, and Bi and the IV-VI compound semiconductors have been found by the fitting of previous calculations and photoemission data. The two-center interactions are found to scale with bond length d. The $pp\sigma$ interaction scales as $d^{-2.6}$ and the $ss\sigma$ interaction as $d^{-4.6}$. In the tetravalent diamond semiconductors both s and p interactions scale as d^{-2}. The different scaling law reflects bonding differences; both s and p electrons are involved in bonding in diamond while only p electrons are used in the group-V and IV-VI compound solids. The states of the group-V elements are reasonably well reproduced with only first-neighbor interactions. Second-neighbor interactions or excited s^* and d^* states are needed to fit the narrow gaps of the IV-VI compound semiconductors. The electronic structure of the rocksalt phase of InSb is also calculated and used to illustrate the differences in bonding between III-V and IV-VI compounds.

I. INTRODUCTION

The tight-binding (TB) method is an increasingly popular way of describing the electronic structure of solids, especially in situations where periodicity is absent, such as in defects, surfaces, and amorphous phases. The interactions of the TB Hamiltonian may be calculated directly but more frequently they are treated as disposable parameters found by fitting some accepted crystalline band structure. Many such fits have been made to the bands of the average valence four, or $\langle 4 \rangle$, semiconductors, the diamond- and zinc-blende-structure crystals. In this paper we present TB band structures for the $\langle 5 \rangle$ crystals, the group-V elements (the pnictides) and the IV-VI narrow-band-gap compound semiconductors, and identify the chemical trends in the interaction parameters.

Harrison has found[1–3] the valence and lower-conduction bands of the $\langle 4 \rangle$ elements can be reasonably well fitted using only nearest-neighbor interactions which were found to scale with bond length d as d^{-2}. Similar scaling with bond length has been found for the valence-band widths and optical excitations of the rocksalt crystals[3,4] which are $\langle 4 \rangle$ insulators. The usual way to fit the bands of an isoelectronic series of compounds is to first fit the bands of the elements where scaling is seen more easily, and then to use these parameters to fit the bands of the polar compounds which have a greater number of disposable parameters. The identification of scaling is more difficult in $\langle 5 \rangle$ crystals than in $\langle 4 \rangle$ crystals because only the three heaviest elements, As, Sb, and Bi, crystallize in the relatively simple $A7$ structure and consequently only a small range of bond lengths is covered without parameters for N and P.

It is our desire that the TB band structures describe both the valence and conduction bands. Generally, a basis of the sp^3 valence orbitals gives adequate valence bands in a variety of materials with only first-neighbor interactions. With increasing ionicity, however, the like-atom second-neighbor terms begin to dominate the effects of the unlike-atom first-neighbor terms, as in the rocksalt crystals.[4] It is found that the introduction of two second-neighbor terms greatly improves the bands of the moderately ionic IV-VI compounds when an sp^3 basis is used.

The addition of an excited s^* orbital to an sp^3 TB basis greatly improves its ability to describe the lower conduction band of $\langle 4 \rangle$ semiconductors, particularly the indirect gap in Si and GaP.[5–7] The use of an s^* orbital and only first-neighbor terms is much more efficient than using a variety of high-order terms within an sp^3 basis. The s^* orbital is believed to represent the effects of nonorthogonality and has only a limited connection to the excited states of the free atom.[8] An excited basis set is particularly efficient for those applications which require the partial density of states (DOS) of both the valence and conduction bands, such as in Green's-function calculations of surface states and deep traps.[5,9]

In the present paper two types of fitted-band structures are given for the IV-VI compounds. The first, more conventional fit, uses a sp^3 basis and includes some second-neighbor interactions. An alternative fit is also presented using excited orbitals and only first-neighbor terms. In contrast to the $\langle 4 \rangle$ semiconductors three excited states, an s^* orbital and two d^* orbitals per site, are included in this method and are used to optimize various band energies at point L. In fact a slightly better fit around point L is possible using the second method. Spin-orbit coupling is not included in the present band structures, as we are primarily interested in trends in their interactions.[9]

II. BANDS FOR GROUP-V ELEMENTS

The atoms in the $A7$ structure have a distorted octahedral coordination, with three close and three more distant bonded neighbors. The structure itself is best considered by referring to an fcc lattice with two atoms per lattice point at (0,0,0) and ($\frac{1}{2}$,0,0) which has undergone a rhombohedral shear along (111) and a relative displacement of each sublattice by $+\beta$ along (111). The corresponding Brillouin zone is a distortion of the truncated octahedral

TABLE I. Orbital energies and two-center interactions for As, Sb, and Bi, in the form V_1 and V_2, in eV.

	r(Å)	$-V(ss)$	$V(sp)$	$V(pp\sigma)$	$-V(pp\pi)$	$-E(s)$	$-E(p)$
As	2.51	1.17	1.60	3.10	0.79	11.0	1.0
	3.15	0.53	0.80	1.66	0.29		
Sb	2.87	0.69	1.14	2.17	0.51	9.0	0.4
	3.37	0.33	0.50	1.25	0.14		
Bi	3.10	0.43	0.78	1.75	0.32	10.8	1.0
	3.47	0.23	0.36	1.09	0.08		

zone of the fcc lattice. The most significant change is that the eight previously equivalent L points have split into two points labeled T, which retain the full trigonal symmetry, and six points of lower symmetry labeled L of lower symmetry.

The bands for the elements are calculated here using an sp^3 basis and retaining only the interactions to the six nearest atoms. Two sets of interactions are needed, one for each bond length. For $ss\sigma$ the two interactions are defined as $V_1(ss\sigma)$ and $V_2(ss\sigma)$, respectively. The actual fitting of the bands is most conveniently described in terms of the symmetric and antisymmetric combinations of these $V_s(ss\sigma)$ and $V_a(ss\sigma)$, defined as the semisum and semidifference of $V_1(ss\sigma)$ and $V_2(ss\sigma)$, respectively. Similar definitions can also be given for the other interactions $V(sp\sigma)$, $V(pp\sigma)$, and $V(pp\pi)$.

The bands and DOS for As, Sb, and Bi are shown in Fig. 1. The two lower bands are s-like and the next six bands are p-like. The parameters are fitted to previous calculations and to experimental x-ray photoemission spectra (XPS).[10] There have been a number of previous calculations for the pnictides: for As by the pseudopotential and orthogonalized-plane-wave (OPW) methods,[11] for Sb using pseudopotentials,[12] and for Bi using pseudopotentials,[13] and the augmented-plane-wave (APW) method.[14] Bullett calculated the TB interactions by the chemical pseudopotential method and obtained the bands DOS for As and Sb.[15]

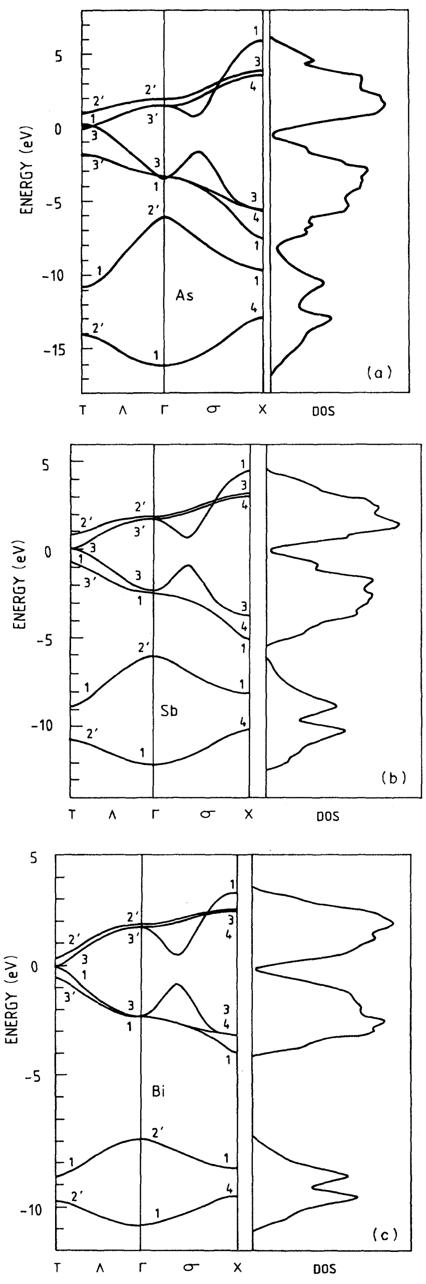


FIG. 1. Band structure of $A7$ As, Sb, and Bi.

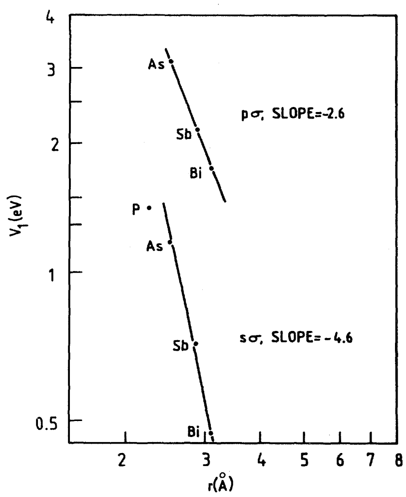
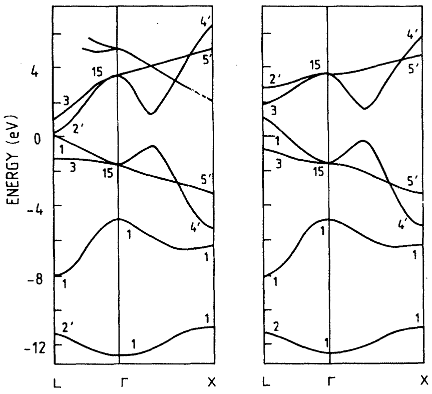


FIG. 2. Bond-length dependence of $V_1(pp\sigma)$ and $V_1(ss\sigma)$.



(a) (b)

FIG. 3. APW bands of SnTe and TB bands without second-neighbor interactions or excited orbitals.

The TB parameters are found by fitting selected energy separations. The pseudopotential calculations are seen to give a p-band width close to that found by XPS, while placing the s bands insufficiently deep. Therefore, the s parameters are fitted only to XPS results while the p parameters are fitted to a combination of XPS and previous calculations. The width of the s band is approximately $6V_s(ss\sigma)$ which sets its size. $V_a(ss\sigma)$ is chosen to give the correct splitting of the doublet in the s-band DOS.[10] The mean position of the doublet is used to set $V_s(sp\sigma)$. The most strongly bound p states are at point X. Their energy below the p level is approximately $2[V_s(pp\sigma)-2V_s(pp\pi)]$ and this is fitted to the XPS width. The individual p parameters are then chosen to reproduce as well as possible the band dispersion along ΓT. The parameters are collected in Table I.[16] Each type of interaction is seen to vary monotonically with bond length along the sequence As, Sb, Bi. The $ss\sigma$ and $pp\sigma$ interactions are plotted against bond length in Fig. 2 to identify any scaling relationships. We find $pp\sigma$ to vary as $d^{-2.6}$ over the limited range of bond lengths available while $ss\sigma$ varies as $d^{-4.6}$.

The scaling behavior of interactions in $\langle 5\rangle$ elements contrasts with that in $\langle 4\rangle$ elements and suggests a difference in bonding. Harrison found[1–3,7] that all interactions varied as d^{-2} in a simple parametrization of the bands of $\langle 4\rangle$ elements and Vogl and Hjalmarson[6] found this to hold relatively well for zinc-blende compounds. The origin of this scaling behavior was traced to the similarity of the TB and free-electron bands of $\langle 4\rangle$ elements.[3] The latter bands automatically scale as the electronic kinetic energy as d^{-2}. The different scaling in the pnictides found in Fig. 2 almost certainly reflects differences in the bonding between $\langle 4\rangle$ and $\langle 5\rangle$ compounds. In $\langle 4\rangle$ zinc-blende compounds the s and p electrons hybridize and are both involved in bonding, while in $\langle 5\rangle$ compounds the bonding is between p electrons only[17,18] leaving the s electrons nonbonding. The p electron density now determines the atomic volume of pnictides and has free-electron-like scaling behavior. In such a situation only the p interactions would scale as d^{-2}. The s orbitals are now smaller than the atomic radius and become progressively more corelike with increasing atomic number. Their interactions decrease more quickly than d^{-2}. The s interactions can be visualized as being mediated by the p electron sea, as happens for the d-d interactions in transition metals.[3,19] The actual dependence of $V(ss\sigma)$ on d may not be a power law but may simply reflect the increased s-p energy splitting with atomic number metallicity,[1] sometimes called a relativistic effect.[20]

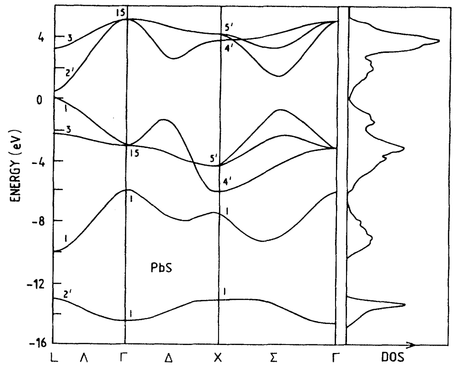


FIG. 4. Second-neighbor TB bands for PbS.

III. IV-VI—SEMICONDUCTOR ENERGY BANDS

The band structures of the IV-VI compounds are in many ways easier to fit than those of the elements because

TABLE II. Universal sp^3 parameters in eV; c is the cation, a is the anion.

	PbTe	PbSe	PbS	SnTe	SnSe	SnS	GeTe	GeSe	GeS
$-V(ss)$	0.41	0.53	0.60	0.47	0.58	0.67	0.57	0.73	0.83
$V(sc,pa)$	0.95	1.05	1.24	0.90	0.99	1.10	0.96	1.10	1.16
$V(sa,pc)$	0.53	0.52	0.48	0.57	0.55	0.48	0.60	0.67	0.73
$V(pp\sigma)$	1.50	1.71	1.81	1.60	1.76	1.91	1.76	1.98	2.12
$-V(pp\pi)$	0.23	0.25	0.27	0.24	0.26	0.28	0.26	0.28	0.31
$V(pc,pc\sigma)$	0.38	0.48	0.50	0.38	0.34	0.30	0.3	0.3	0.3
$V(pa,pa\sigma)$	0.03	0.03	0.07	0.08	0.07	0.07	0.03	0.03	0.03
	Pb	Sn	Ge	Te	Se	S			
$-E(s)$	15.5	14.6	15.4	18.0	20.6	20.8			
$-E(p)$	5.77	5.94	6.36	8.60	9.53	10.27			

TABLE III. Universal $sp^3s^*d^2$ parameters in eV.

	PbTe	PbSe	PbS	SnTe	SnSe	SnS	GeTe	GeSe	GeS	InSb
r(Å)	3.26	3.06	2.97	3.16	3.00	2.89	3.01	2.83	2.74	3.06
$-V(ss)$	0.41	0.53	0.60	0.47	0.58	0.67	0.57	0.73	0.83	0.84
$V(sc,pa)$	0.82	0.91	0.97	0.98	1.07	1.15	0.97	1.09	1.16	1.26
$V(sa,pc)$	0.59	0.49	0.41	0.70	0.72	0.74	0.87	0.92	0.98	0.96
$V(pp\sigma)$	2.02	2.30	2.44	2.15	2.39	2.57	2.37	2.68	2.86	2.37
$-V(pp\pi)$	0.38	0.43	0.46	0.40	0.45	0.48	0.44	0.55	0.54	0.53
$V(s^*c,pa)$	0.95	0.93	0.84	1.06	1.1	1.1	1.13	1.15	1.15	1.53
$V(s^*a,pc)$	1.38	1.40	1.46	1.24	1.25	1.25	1.24	1.25	1.25	0.50
$V(d^*c,pa)$	1.49	1.73	1.76	1.81	1.8	1.8	1.58	1.6	1.6	1.77
$V(d^*a,pc)$	0.99	0.88	0.96	1.16	1.2	1.2	1.48	1.5	.5	1.57
$E(s,c)$	−7.50	−7.40	−7.20	−6.6	−5.77	−5.6	−7.7	−6.4	−6.1	−3.27
$E(p,c)$	3.38	3.07	2.53	1.73	1.66	2.60	1.83	2.39	3.67	4.32
$E(s^*,c)$	8.8	8.8	8.2	9.0	7.2	7.4	10.0	7.7	7.7	10.9
$E(d^*,c)$	8.5	8.5	8.1	8.6	7.1	7.3	9.7	7.6	7.5	10.9
$E(s,a)$	−11.5	−13.9	−14.6	−12.0	−13.8	−12.3	−11.3	−11.6	−12.0	−7.77
$E(p,a)$	0.13	−0.25	−0.68	−0.15	−0.47	−0.81	0.07	−0.29	−0.74	2.00
$E(s^*,a)$	8.8	8.3	8.0	8.3	7.0	7.2	9.4	7.5	7.4	10.8
$E(d^*,a)$	8.6	8.2	8.4	8.1	6.9	7.1	9.3	7.4	7.3	10.7

five of them, GeTe, SnTe, PbTe, PbSe, and PbS, all possess a rocksalt phase. Exact algebraic expressions can be derived for TB band energies at points of high symmetry, Γ, X, and L. It is necessary to define s and p orbital energies for the cation and anion, $E(s,c)$, $E(p,c)$, $E(s,a)$ and $E(p,a)$, and also to distinguish between the two $sp\sigma$ interactions, $V(sc,pa)$ and $V(sa,pc)$, the former with the s orbital on the cation. Two second-neighbor interactions are retained, $V(pc,pc\sigma)$ and $V(pa,pa\sigma)$ between cations and anions, respectively. In the alternative procedure the excited orbitals are only allowed to interact with p orbitals, as in ⟨4⟩ compounds,[5] so there are two additional sets of ps^* and pd^* parameters.

The importance of these extra terms is seen in Fig. 3, where the TB bands are compared to the APW bands of SnTe.[21] Figure 3(b) shows the TB bands without second-neighbor or excited orbital interactions. It is clear that the states at points Γ and X are quite well described but those at point L are in the incorrect order; the singly degenerate L_1 and L_2' states are too high in energy due to repulsion by the lower s orbitals. As the minimum gap is at point L, it is preferable to describe this region correctly, particularly for any application that requires accurate conduction bands, such as for deep traps. The L_1 and L_2' states can be lowered by including second-neighbor $pp\sigma$ parameters which raise the average p energies at point Γ and lower the L_1 and L_2' states.

Alternatively, band structures may be calculated using an expanded basis set. Bands retain atomic symmetries at point Γ. Thus we can arrange that only zone-edge states are moved by only allowing interactions between orbitals of different symmetry. Including s^*p interactions in the

TABLE IV. Ionicities calculated with the parameters of Table III compared to those of other workers.

	Present work	Kemeny[a]	Schiferl[b]	BOM[c]
GeS	0.50	0.50	0.65	
GeSe	0.36	0.55	0.59	
GeTe	0.28	0.66	0.49	0.38
SnS	0.47	0.61	0.76	
SnSe	0.35	0.69	0.72	
SnTe	0.35	0.75	0.64	0.48
PbS	0.54	0.67	0.79	0.63
PbSe	0.50	0.70	0.76	0.61
PbTe	0.43	0.74	0.65	0.55
InSb (rocksalt structure)	0.26			
InSb (zinc-blende structure)	0.22			

[a] See Ref. 31.

[b] See Ref. 36.

[c] Bond-orbital model (BOM), see Ref. 38.

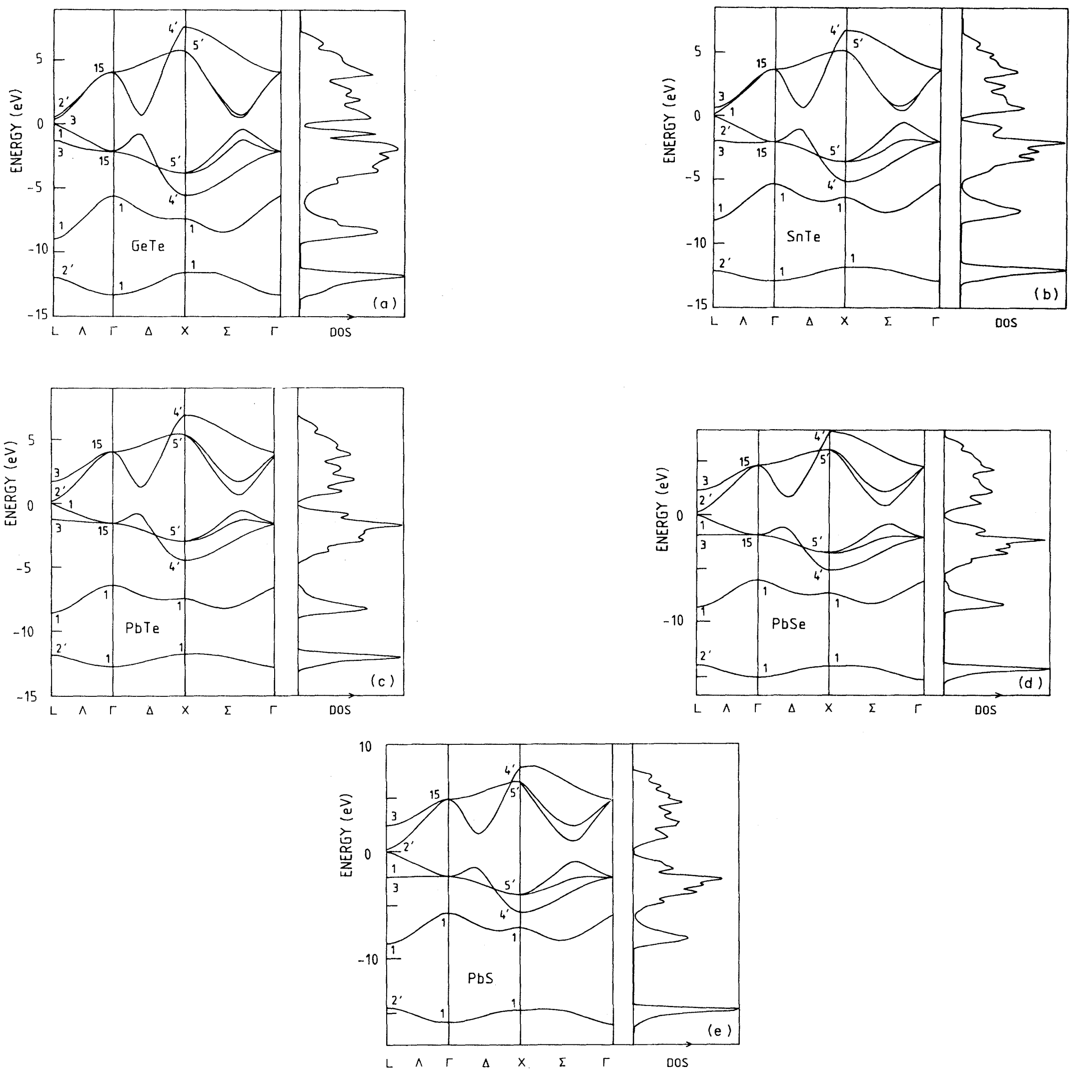


FIG. 5. $sp^3s^*d^2$ TB bands and DOS for GeTe, SnTe, PbTe, PbSe, and PbS.

zinc-blende lattice moves the X_1 state downward and, to a smaller extent, also moves states at point L. In the rock-salt lattice, including an s^*p, interaction moves the L_1 and L_2' states downward, leaving states at both points Γ and X unchanged, as desired. Figure 3(b) shows that the L_3 states are also too high in a first-neighbor fit. These states have pure $p_{\parallel}$ character.[18] These may be lowered by a repulsion by d^* orbitals. If only first-neighbor $V(p,d^*)$ type interactions are retained, then only two of the five d orbitals, the $d_{x^2-y^2}$ and $d_{3z^2-r^2}$, interact with the $p_{\parallel}$ states. Only these two are retained, expanding our Hamiltonian from 8×8 to 14×14—sp^3 to $sp^3s^*d^{*2}$. Using the various interactions, the positions of all the lowest eight states at point Γ, the lowest five at point X, and the lowest eight at point L can be individually fitted in the $sp^3s^*d^{*2}$ scheme. The first major failure is for the X_4 state which is pure d-like, but no attempt was made to fit it with our d basis.

The accuracy of the various band calculations[21–25] can be compared using photoemission data.[26–31] The angle-resolved photoemission (ARPES) data of Grandke *et al.*[26] provides a very valuable test of the calculated dispersions of the valence p bands, bands 3–5. The authors conclude that in general the OPW calculations[22] fare well, but the local empirical pseudopotential method[23] (EPM) results are not so good, especially for PbTe. The nonlocal EPM results[24] which were fitted to XPS and ultraviolet photoemission (UPS) data[27,28] were shown to be good for PbTe, but the results seriously overestimate the bandwidth of PbSe.[26] This trend was also found in our preliminary fits; a much larger value of $V(pp\sigma)$ was found when fitting the latter bands. There are no ARPES data for the s-like bands 1 or 2, but their mean positions can be found from UPS and XPS data.[27–31] Generally, it is found that both bands are placed too high even in the OPW results[22] and we also found little regularity in the $ss\sigma$ parameters. It is probable that the OPW and local EPM calculations have difficulty describing the *s* bands.

Our final TB band structures for the rocksalt IV-VI compounds were derived, as for the elements, by combining fits to the OPW bands and to the ARPES, UPS, and XPS data. The dimensionless $pp\sigma$ interaction $\eta_{pp\sigma}=V(pp\sigma)d^2$ was remarkably constant in our preliminary fits to the OPW bands,[22] varying by only 4%. Thus the $V(pp\sigma)$ and $V(pp\pi)$ interactions are taken to scale as d^{-2} using the mean values of $\eta_{pp\sigma}$ and $\eta_{pp\pi}$. The elemental values of Fig. 2 were used for the $V(ss\sigma)$. The *s* orbital energies were shifted to fit their XPS band positions. The $V(s,p)$ parameters were adjusted to give the same Γ-L band dispersions as in the OPW results, including the inverted symmetry of gap states at point L in SnTe as a constraint.[21] However, it was not possible to include the inversion of conduction-band symmetries at point L in PbTe (Refs. 32 and 33) as a constraint without causing a deterioration in the fit for other compounds. The second-neighbor sp^3 parameters are given in Table II and the bands for PbS are shown in Fig. 4. The $sp^3s^*d^2$ parameters and the five fcc band structures are shown in Table III and Fig. 5, respectively. Overall, the $sp^3s^*d^2$ bands are perhaps better, having wide conduction bands and more accurate L_3 states. However, one should note that if only first-neighbor interactions are permitted in either the rocksalt or zinc-blende lattice, there are insufficient harmonic components to break the degeneracy between states at $X(100)$ and $W(1\ \frac{1}{2}\ 0)$, no matter how many excited states are included.

Now that a single, consistent set of interactions is available, the calculations can be extended to those compounds which do not have a rocksalt phase—SnSe, SnS, GeSe, and GeS. Here, we have calculated the DOS for their hypothetical rocksalt phases as seen in Fig. 6; elsewhere it is planned to calculate the band structures in the actual rhombohedral or orthorhombic structures. The DOS of the *s* bands is almost independent of crystal symmetry, unlike that of the *p* bands,[34,35] so these may be compared to XPS.[30] The bond lengths were derived by assuming that the unit cell volumes were independent of the rhombohedral or orthorhombic distortions.[36] The sp^3 parameters of Table II were used for the results of Fig. 6. The orbital energies are referenced to a vacuum level to emphasize that we have produced a single set of parameters for use in all the IV-VI compounds, whatever their structure. Two-center parameters for the distorted phases should be calculated by scaling. We also give parameters for rocksalt phase of GeS, etc., in Table III for the $sp^3s^*d^2$ scheme, but for the moment the sp^3 scheme is preferred for the distorted phases until the effects of the loss of symmetry on the overlap and the excited orbitals can be assessed.

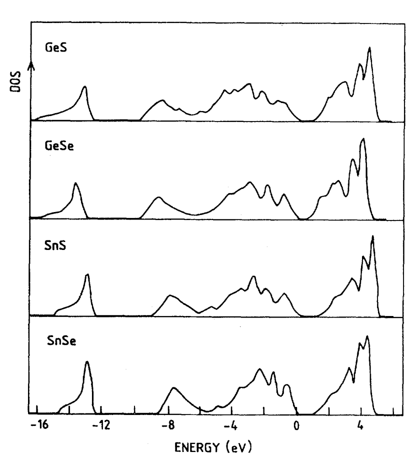


FIG. 6. DOS for the fcc phases of GeS, GeSe, SnS, and SnSe.

The bands of all the IV-VI compounds are broadly similar, the main difference is that the DOS peak of the fifth valence band is separated from the lower peak in PbS and PbSe. This is largely due to the lower *p* energies of S and Se compared to Te. The $p_{\parallel}$ orbitals form bands 3 and 4 and are repelled downward by the cation *p* states, leaving band 5 relatively higher. This band is formed from anion $p_{\perp}$ states which are repelled upward by the cation *s* states concentrated in band 2.

We also fitted the bands[37] of the rocksalt phase on InSb, shown in Fig. 7. This is the metallic phase of a III-V compound whose electronic structure throws some light on the bonding and ionicity in both the zinc-blende-structure III-V compounds and the rocksalt-structure IV-VI compounds.

Ionicities may be calculated for the $\langle 5\rangle$ compounds using the TB electronic charge densities. Both the cation and anion *s* orbitals are found to be almost completely occupied, confirming that only *p* bonding occurs. Hence ionicities are calculated from the occupancies of the three *p* orbitals only. The ionicity or polarity f_i is defined as the asymmetry of the valence charge, as in $\langle 4\rangle$ compounds.[1] The net atomic charge is the sum of this valence charge asymmetry and the core charge asymmetry, which is ±1 for IV-VI compounds. All four sp^3 orbitals participate in bonding in the III-V compounds and are included in the ionicity calculation. In the IV-VI compounds, the metal and chalcogen *s* orbitals are almost completely occupied, so ionicities were calculated in terms of *p* orbital occupancies only. The resultant ionicities are compared in Table IV with those found by other methods. Overall our ionicities are much smaller than commonly quoted for IV-VI compounds, but they vary in a similar manner to those of Schiferl[36] and from the bond-orbital model,[38] but not from those of the XPS *s* band positions.[31] The ionicities of IV-VI compounds should not be very large as there is only a valence difference of two. The ionicities of IV-VI compounds are greater than that of rocksalt-phase

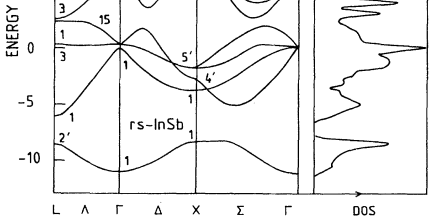


FIG. 7. Fitted $sp^3s^*d^2$ bands and DOS of rocksalt-structure InSb.

InSb which in turn is greater than that of zinc-blende phase InSb. This emphasizes that the covalence of the octahedral rocksalt structures is weaker than that of zinc-blende and that *p* electron covalence is weaker than the sp^3 covalence of the III-V compounds. The results also emphasize that the ionicities of IV-VI compounds are for *p* electrons not *s* electrons as measured by XPS.[31] $V(ss)$ of rocksalt-phase InSb is larger than that of PbSe presumably because its *s* states participate in bonding. Also, its occupied states have a larger content of excited states due to the metallic nature of rocksalt-phase InSb. Although ionicities are frequently used to classify the crystal structures of isoelectronic compounds,[20] and indeed this has been attempted for the IV-VI compounds,[31,36] our values are not suitable for this. The quantum-defect parameters are better suited for this application.[39]

In summary, fitted TB band structures have been presented for the $\langle 5 \rangle$ elements and compounds using various schemes. It was found that $pp\sigma$ interactions scale with bond length roughly as d^{-2}, while the $ss\sigma$ interactions vary more rapidly, a result of the *p* bonding of these compounds. It was possible to produce very close fits to the bands of IV-VI compounds. The parameters found can be used in conjunction with scaling rules to calculate the electronic structures of those IV-VI compounds not having fcc phases. Finally, ionicities were calculated and used to illustrate differences in bonding in III-V and IV-VI compounds.

ACKNOWLEDGMENTS

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