

Role of d Orbitals in Valence-Band Offsets of Common-Anion Semiconductors

Su-Huai Wei and Alex Zunger

Solar Energy Research Institute, Golden, Colorado 80401

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We show through all-electron first-principles electronic structure calculations of core levels that, contrary to previous expectations, the valence-band offsets in the common-anion semiconductors AlAs-GaAs and CdTe-HgTe are decided primarily by intrinsic bulk effects and that interface charge transfer has but a small effect on these quantities. The failure of previous models is shown to result primarily from their decision to omit cation d orbitals.

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Measurements¹⁻³ and theoretical modeling⁴⁻⁷ of the lineup between the top of the valence bands of two semiconductors forming a heterojunction have recently been revived⁸ in light of new results which cast doubt on both previous measurements⁹ and theories.^{4,5} Textbook descriptions¹⁰ of the zone-center valence-band maximum (VBM) in a binary zinc-blende semiconductor (the Γ_{15c} state) suggest that it consists almost exclusively of anion valence p orbitals. It was therefore initially expected^{4,5,8-11} that the VBM energies of two common-anion semiconductors which share the same crystal structure and lattice constant (e.g., the AlAs-GaAs or CdTe-HgTe pairs), would be nearly equal. These expectations were formulated in terms of the hitherto successful "common-anion rule"¹¹ (stating that the offset ΔE_{VBM} between the VBM energies of two covalent semiconductors reflects primarily different anion energies, and hence would nearly vanish for semiconductors sharing a common anion), and simple tight-binding⁴ and dielectric⁵ models, all predicting nearly vanishing (< 0.1 eV) band offsets for such common-anion systems. While these predictions were in agreement with the then-available experimental data on AlAs-GaAs (Ref. 9) and HgTe-CdTe,¹² more recent measurements on AlAs-GaAs [$\Delta E_{\text{VBM}} = 0.45 \pm 0.05$ eV (Ref. 2)] and CdTe-HgTe ($\Delta E_{\text{VBM}} = 0.35 \pm 0.06$ eV (Ref. 1)] have shown previous expectations and models to be substantially in error. It has been recognized,^{8,13} however, that the band offset ΔE_{VBM} could be thought to consist of an intrinsic "bulk" (b) contribution ΔE_{VBM}^b , reflecting the disparity between the VBM energies of two *isolated* semiconductors (when their energies are compared on the same, absolute scale), and an "interface specific" (IS) contribution $\Delta E_{\text{VBM}}^{\text{IS}}$ reflecting chemical events at the *interface* (hence, depending on interfacial charge transfer, orientation, dipole layer, interdiffusion, defect structure, etc.):

$$\Delta E_{\text{VBM}} = \Delta E_{\text{VBM}}^b + \Delta E_{\text{VBM}}^{\text{IS}}. \quad (1)$$

The failure of previous models^{4,5} in the crucial common-anion test was recently interpreted^{4c,6} as reflecting the neglect of $\Delta E_{\text{VBM}}^{\text{IS}}$ —in particular the omission of interfacial charge-transfer (screening) effects. This inter-

pretation granted a decisive physical role to interfacial dipoles in establishing ΔE_{VBM} for these systems.

In this Letter we contest this basic physical interpretation. We first calculate the valence-band offsets of the four basic common-anion semiconductors AlAs-GaAs, CdTe-HgTe, CdTe-ZnTe, and HgTe-ZnTe in a way that parallels their measurement in photoemission core-level spectroscopy^{1,3}: from the core levels. We find our calculated ΔE_{VBM} values to be in good agreement with experiment. We then use a simple electrostatic model for core shifts to show that interface-specific dipole contributions to ΔE_{VBM} are small in these systems. We show furthermore that the failure of earlier models^{4,5} does not result primarily from neglect of $\Delta E_{\text{VBM}}^{\text{IS}}$, but is predominantly a consequence of imperfect representation in simple tight-binding models^{4,10} of ΔE_{VBM}^b . In particular, the omission of the outermost *cation* d orbitals explains most of the incorrect magnitudes.⁴ This approach hence provides a fundamentally different interpretation of the physical mechanism governing band lineups in common-anion systems, and provides a simple correction which fixes previous models.⁴ Predictions for band lineups for two hitherto unreported systems (CdTe-ZnTe and ZnTe-HgTe) are given.

We begin by reviewing the tight-binding viewpoint on the problem. In this approach^{4,10} the energy of the Γ_{15c} VBM of a zinc-blende semiconductor AC is expressed solely in terms of nonmetal (C) and metal (A) p -orbital atomic energies (ϵ_p^C and ϵ_p^A , respectively) and their interaction (V_{pp}) as

$$\epsilon_{\text{VBM}}^{\text{AC}} = (\epsilon_p^A + \epsilon_p^C)/2 - [(\epsilon_p^A - \epsilon_p^C)^2/4 + V_{pp}^2]^{1/2}. \quad (2)$$

The bulk-intrinsic ("natural"⁴) valence-band offset between two semiconductors AC and BC is then simply given as the difference between the respective VBM energies as

$$\Delta E_{\text{VBM}}^b = \epsilon_{\text{VBM}}^{\text{BC}} - \epsilon_{\text{VBM}}^{\text{AC}}. \quad (3)$$

The charge-transfer term is approximated as the difference^{4c}

$$\Delta E_{\text{VBM}}^{\text{IS}} = \epsilon_h^{\text{AC}} - \epsilon_h^{\text{BC}} \quad (4)$$

TABLE I. Tight-binding, all-electron, and experimental valence-band offsets (in electronvolts) in common-anion pairs, calculated from different core levels (nl). SO is the spin-orbit splitting.

Systems	Tight-binding ^a				Average (with SO)	Average (no SO)	All-electron (Present results)			δ_{pd}
	ΔE_{VBM}^b	ΔE_{VMB}^{1S}	ΔE_{VMB}^{1P}	ΔE_{VMB}^{3P}			Using 1s	Using 2s	Using 3p _{1/2}	
CdTe-HgTe	0.00	0.09	0.09	0.35 ± 0.06^b	0.37	0.39	0.377	0.388	0.400	0.34
CdTe-ZnTe	-0.07	0.00	-0.07	...	0.13	0.12	0.125	0.122	0.108	0.04
ZnTe-HgTe	0.07	0.09	0.16	...	0.26	0.29	0.277	0.286	0.289	0.30
AlAs-GaAs	0.01	0.15	0.16	0.45 ± 0.05^c	0.42	0.41	0.41	0.40	...	0.31

^aUsing data from Ref. 14.

^bReference 1.

^cReference 2.

between the average s - p hybrid energies ϵ_h of the semiconductor AC ,

$$\epsilon_h^{AC} = (\epsilon_s^A + 3\epsilon_p^A + \epsilon_s^C + 3\epsilon_p^C)/8, \quad (5)$$

and that of BC . From Eqs. (1)–(5), Table I¹⁴ exhibits the following features of the tight-binding band offsets: (i) Relative to experiment, the calculated ΔE_{VBM}^b is far too small [reflecting the fact that the differences of p -orbital energies^{4,10,14} for (Zn,Cd,Hg) and (Al,Ga) are small too], and may even have the wrong sign (CdTe/ZnTe), and (ii) the charge-transfer correction of Eq. (4) improves the results but still falls short (by a factor of 2–4) of experiment. For InAs-GaAs,^{4c} not depicted here,¹⁴ dipole effects alone incorrectly reverse the sign of ΔE_{VBM}^b , yielding $\Delta E_{VBM} = -0.13$ eV, whereas the experimental result (quoted in Ref. 4c) is positive (+0.17 eV).

The reader should note at this point that it has long been customary, both in tight-binding⁴ [Eqs. (2) to (5)] and in empirical¹⁵ or first-principles⁷ pseudopotential calculations for semiconductors, to neglect cation d bands, despite the fact that they reside inside¹⁶ the valence band (for II-VI's) or close to its minimum (for III-V's). These cation d bands may, however, *selectively* alter the VBM energies of such compounds, and hence contribute to the band offset between two materials. Observe that in tetrahedral symmetry the cation d and anion p states share the same symmetry representation (Γ_{15}), and hence can interact through the potential matrix element $\langle \phi_A^d | V | \phi_B^p \rangle = V_{dp}$. This interaction repels the VBM by $V_{dp}^2/(\epsilon_p^C - \epsilon_d^A)$. This repulsion varies significantly from one compound to another since both the variations in spatial distributions of the cation d orbitals (hence, V_{dp}) and the variations in the energy denominator ($\epsilon_p^C - \epsilon_d^A$) along the II-VI series are substantial (for ZnTe, CdTe, and HgTe the atomic-orbital energy difference¹⁴ $\epsilon_p^C - \epsilon_d^A$ is 4.3, 5.8, and 3.9 eV, respectively; the energies of the Γ_{15d} d band relative to the VBM are 7.3, 8.4, and 7.4 eV, respectively). Such p - d repulsion effects have been previously shown to reduce significantly the band gaps of II-VI's,¹⁶ to explain the

“band-gap anomaly” in chalcopyrites,¹⁷ and to clarify the reason why Cu impurity acceptor states (exhibiting p - d repulsion) are abnormally deep in II-VI's relative to the isovalent Na impurity¹⁷ (which lacks p - d repulsion). We will show below that this effect also controls much of the band offsets in common-anion semiconductors, and that alternative contributions (e.g., charge transfer) are negligibly small.

We have calculated self-consistently the band structures of ZnTe, CdTe, HgTe, AlAs, and GaAs, treating core states relativistically and valence orbitals semirelativistically, using the general potential linear augmented plane-wave method¹⁸ in the local-density formalism. For each common-anion pair, we also calculated the band structure of the 50%-50% ordered compounds CdHgTe₂, CdZnTe₂, HgZnTe₂, and GaAlAs₂ in the ordered CuAu-I-like structure¹⁹ [space group D_{2d}^5 , identical to an alternating monolayer superlattice in the (001) orientation] to find the cation core-level difference [see Eq. (6) below]. All structural parameters of the ternary compounds^{17,19} are relaxed to attain the minimum total energy.

To parallel the measurement of ΔE_{VBM} in photoemission core-level spectroscopy^{1,3} ΔE_{VBM} is expressed as¹ (see Fig. 1)

$$\Delta E_{VBM} \cong (\epsilon_{VBM}^{AC} - \epsilon_{nl,A}^{AC}) - (\epsilon_{VBM}^{BC} - \epsilon_{nl,B}^{BC}) + (\epsilon_{nl,A}^{ABC_2} - \epsilon_{nl,B}^{ABC_2}). \quad (6)$$

Here, for example, $\epsilon_{nl,A}^{AC}$ is the core level nl of atom A in AC and ϵ_{VBM}^{AC} is the VBM energy of AC . The first two bracketed terms in Eq. (6) are calculated from core levels nl obtained from the band structures of AC and BC , respectively, whereas the third term is calculated from the band structure of ABC_2 . We assume (and demonstrate below) that the core-level difference ΔE_{CL} [last bracketed term in Eq. (6)] in common-anion superlattices (which include information on ΔE_{VBM}^{1S}) has but a negligible dependence on the superlattice thickness. We hence calculated ΔE_{CL} from a simple (1,1) superlattice ABC_2 . This assumption reflects the fact that for

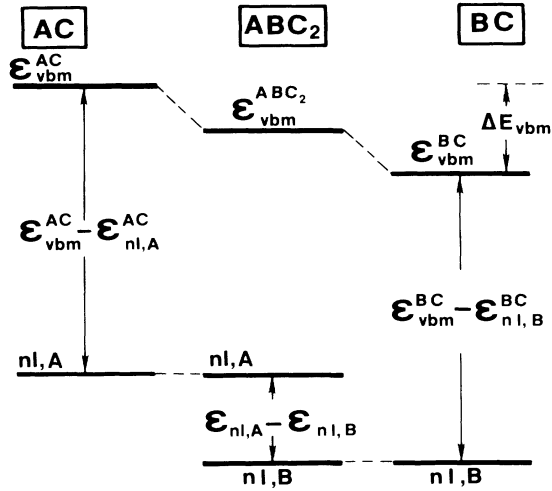


FIG. 1. Schematic energy-level diagram used to deduce the valence-band offset between AC and BC .

common-anion systems interface-induced effects are both small (see discussion below) and localized near the interface. The band offsets calculated from Eq. (6) for different choices of the core levels nl are shown in columns 7–10 of Table I. They exhibit a near independence of ΔE_{VBM} on the core level chosen. Table I also shows that the ΔE_{VBM} values are transitive, i.e., $\Delta E_{VBM}(AC-BC) = \Delta E_{VBM}(AC-DC) + \Delta E_{VBM}(DC-BC)$ to within a precision of 0.02 eV. We test independently our assumption that ΔE_{CL} in common-anion systems is insensitive to the details of the superlattice structure by comparing ΔE_{CL} calculated from the ABC_2 system to that calculated from the A_3BC_4 or AB_3C_4 systems, where the ternary phases are represented in the T_d^I “luzonite” structure.¹⁹ We find these values to agree within 0.02 eV. The fifth and sixth columns of Table I compare the calculated ΔE_{VBM} values [including spin-orbit interactions]²⁰ with experiment,^{1,2} showing nearly perfect agreement for the two cases where data are currently available, and offering two predictions where they are not.

We have suggested (see also Ref. 13) that the deep core levels of *cations* in common-anion pairs are nearly unchanged relative to a *common reference energy* (e.g., vacuum) in going from a binary to a ternary (including alloy¹³) system, i.e.,

$$\epsilon_{nl,A}^{AC} \cong \epsilon_{nl,A}^{ABC_2}, \quad \text{and} \quad \epsilon_{nl,B}^{BC} \cong \epsilon_{nl,B}^{ABC_2}.$$

This “new common-anion rule” can be deduced by calculation of the change $\Delta \bar{V}_A$ in the electrostatic potential at the cation site A upon replacement of one cation (A) in the binary A_2C_2 system by another (B), producing thereby the (1,1) superlattice $AC-BC$ (i.e., ABC_2). This electrostatic potential involves two (competing) contributions: (i) the intersite Madelung potential produced at A

by all other charges and (ii) the on-site Coulomb repulsion due to the altered charge at A . Denoting by $\Delta q = (q_B^{BC} - q_A^{AC})/2$ and $\Delta Q = (q_B^{ABC_2} - q_A^{ABC_2})/2$ the cation charge disparities in the binary compound (BC, AC) and in ABC_2 , respectively, and by d the nearest-neighbor anion-cation distance (assumed equal in the lattice-matched AC and BC semiconductors), the change of the electrostatic potential at A is calculated to be

$$\Delta \bar{V}_A = (\Delta q/d)[\alpha^* \lambda - \alpha_{zB} + (d/R_A)(1 - \lambda)], \quad (7)$$

where $\alpha_{zB} = 1.638$ and $\alpha^* = 0.976$ are the Madelung constants for the zinc blende and for the cation lattice¹⁹ in ABC_2 structures, respectively, $\lambda = \Delta Q/\Delta q$, and R_A is the effective radius for atom A where the charge transfer (in forming ABC_2) occurs.²¹ Our self-consistent calculations show that the charge differences inside the muffin-tin spheres are $\Delta q = 0.024e$, $\lambda = 0.86$ for CdTe-HgTe and $\Delta q = 0.043e$, $\lambda = 0.82$ for AlAs-GaAs. Using the experimental bond lengths ($d = 2.80 \text{ \AA}$ for CdTe and HgTe; $d = 2.45 \text{ \AA}$ for AlAs and GaAs) and estimating²² R_A as $\approx 0.3d$ we find $\Delta \bar{V}_A$ to be as small as 0.04 eV. This small value (comparable to the uncertainty of the calculation and experimental error bars¹⁻³ for ΔE_{VBM}) suggests that interface dipole contributions to ΔE_{VBM} are equivalently small, and justify the use of a thin (1,1) superlattice. It is further supported by recent experimental observations²³ [note that if $\Delta \bar{V}_A = 0$, any size of the superlattice will give the same ΔE_{CL}].

Since the difference between the two cations is the only factor distinguishing any pair of lattice-matched common-anion binary semiconductors, the substantial ΔE_{VBM} values obtained here for AlAs-GaAs and HgTe-CdTe necessarily reflect participation of *cation* orbitals in the VBM. We find that the cation d orbitals, omitted in previous studies^{4,7} are the major contributors. *First*, our self-consistent band calculations show directly substantial hybridization of cation d character in the Γ_{15c} VBM state: Within the cation muffin-tin sphere we find 7.5%, 6.9%, and 12.2% d character for Γ_{15c} of ZnTe, CdTe, and HgTe, respectively. [For comparison, note that the cation p character (4.3%, 4.0%, and 4.0%, respectively) is actually lower than the d character in the II-VI systems!] *Second*, one can independently model the amount ΔE_{pd}^{AC} by which the VBM of AC is repelled upwards by the cation d band, and hence find the pd correction $\delta_{pd} = \Delta E_{pd}^{BC} - \Delta E_{pd}^{AC}$ to the band offset between BC and AC . ΔE_{pd}^{AC} can be obtained as the amount by which the Γ_{15a} cation- d -band energy shifts upwards as anion p orbitals are removed from the linear augmented plane-wave basis set. Alternatively, one can calculate ΔE_{pd}^{AC} by subtracting from the total $\Gamma_{15c}-\Gamma_{1c}$ valence-band width (calculated with cation d bands) the corresponding tight-binding value (calculated without cation d bands). Both models yield to within ± 0.1 eV the δ_{pd} corrections to the band offsets 0.04, 0.34, 0.30, 0.31, 0.04, and 0.35 eV for the CdTe-ZnTe, CdTe-HgTe,

ZnTe-HgTe, AlAs-GaAs, GaAs-InAs, and AlAs-InAs pairs, respectively. Note that δ_{pd} is large for Hg-containing semiconductor pairs (since the Hg 5d orbitals are shallower than other column-II cation d orbitals, and hence repel the VBM more effectively) and for Al-containing compounds (since the empty Al 3d orbitals are higher in energy than the anion p orbitals, and hence ΔE_{pd} is negative). For all other common-anion pairs ΔE_{pd}^A is similar, and hence the tight-binding model is expected to work well for these systems.

In conclusion, we find that the principal error in previous tight-binding models for band lineup in lattice-matched compounds (and to a lesser extent also in plane-wave pseudopotential models⁷ which also neglect occupied cation d bands) is omission of cation d orbitals, and that the assertion that interface dipole effects are needed to obtain the correct lineup is not tenable.

After the results of this work were circulated privately, Duc, Hsu, and Faurie informed us of their new photoemission measurements²⁴ of the band offsets in CdTe-ZnTe (0.10 ± 0.06 eV) and ZnTe-HgTe (0.25 ± 0.05 eV), in excellent agreement with our independent predictions of Table I.

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¹⁴We evaluate the tight-binding expressions of Eqs. (2)-(5) using semirelativistic local-density orbital energies calculated with the Hedin-Lundqvist exchange correlation. The input data are s energies -15.43, -6.31, -6.04, -7.21, -14.77, -7.91, -9.25, and -8.56 eV; and p energies -6.19, -1.31, -1.41, -1.26, -5.42, -2.86, -2.82, and 2.78 eV for Te, Zn, Cd, Hg, As, Al, Ga, and In, respectively. V_{pp} is taken from Ref. 4c. Combination of relativistic with nonrelativistic (Hartree-Fock) orbital energies (Ref. 4c) has previously produced erroneous results for the CdTe-HgTe pair. Relativistic orbital energies produce better results for GaAs-InAs than those given in Ref. 4c.

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²⁰The spin-orbit-corrected ΔE_{VBM} is obtained by our adding $\Delta_0/3$ to each compound, where Δ_0 is the calculated spin-orbit splitting at VBM. The calculated Δ_0 are 0.89, 0.87, 0.79, 0.34, and 0.30 eV for ZnTe, CdTe, HgTe, GaAs, and AlAs, respectively.

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²²In estimating the charge transfer radius R_A we note that, in the formation of ABC_2 from $AC+BC$, the charge transfer ($\Delta q - \Delta Q$) occurs on the cation sublattice. Since cation radii are smaller than anion radii in these systems, $R_A < d/2$.

²³C. K. Shih, J. A. Silberman, A. K. Wahi, G. P. Carey, I. Lindau, W. E. Spicer, and A. Sher [Proceedings of the U.S. Workshop on Mercury Cadmium Telluride, Dallas, TX, October 1986, edited by G. Lucovsky, J. Vac. Sci. Technol. A (to be published)] have indeed observed that if cation core levels are assumed to be unshifted in the alloying process ($\Delta \bar{V}_A \cong 0$), the composition variation of the energy difference between VBM and core level in the $Hg_{1-x}Cd_xTe$ system gives the same band offset as that measured directly (Ref. 1).

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