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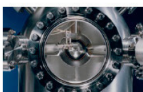


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Calculation of the valence band offsets of common-anion semiconductor heterojunctions from core levels: The role of cation *d* orbitals

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The valence band offsets of the common-anion CdTe–HgTe, CdTe–ZnTe, ZnTe–HgTe, and GaAs–AlAs semiconductor pairs are calculated from the core level energies. The good agreement obtained with experiment for lattice-matched systems and a simple electrostatic model analysis suggest interface dipoles to have only a small effect. Furthermore, the microscopic origin of the failure of the common-anion rule in lattice-matched systems is identified: it is found that participation of *cation d orbitals* (neglected by tight-binding and pseudopotential approaches alike) in the valence band maxima is responsible for much of the band offset in these systems.

I. INTRODUCTION

The offset ΔE_{VBM} between the valence band maxima (VBM) of two semiconductors A and B forming a heterostructure is one of the most important device parameters of interfacial structures.¹ It can be decomposed into an intrinsic “bulk” (b) contribution ΔE_{VBM}^b characteristic of the two separated systems A and B, and an “interface specific” (is) contribution $\Delta E_{\text{VBM}}^{\text{is}}$ which depends on the properties of the A–B interface²:

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

By definition, ΔE_{VBM}^b is both linear in its constituent components [$\Delta E_{\text{VBM}}^b(\text{A/B}) = f(\text{B}) - f(\text{A})$] and transitive [$\Delta E_{\text{VBM}}^b(\text{A/B}) = \Delta E_{\text{VBM}}^b(\text{A/D}) + \Delta E_{\text{VBM}}^b(\text{D/B})$]. In contrast, $\Delta E_{\text{VBM}}^{\text{is}}$ need not share these properties, as it depends on the A–B bond at the interface (hence on the crystallographic orientation, interfacial strain, charge transfer, interdiffusion, defect structure, presence of an oxide layer, etc.). Interestingly, it was empirically observed^{3,4} that the data base of either measured³ or calculated⁴ $\Delta E_{\text{VBM}}(\text{A/B})$ values for a series of A–B semiconductor pairs could be approximately represented in a linear and transitive form $F(\text{B}) - F(\text{A})$, where the F 's are determined empirically by fitting either the experimental³ or calculated⁴ values. While the error in such linear representations (≤ 0.15 eV) is not negligible, the scatter in the measured ΔE_{VBM} values itself is often a sizable fraction of this error. This suggests that useful approximations to ΔE_{VBM} (and indeed an understanding of its underlying mechanism) could be sought by identifying an *a priori* measurable and/or calculable characteristic energy F for each compound, such that

$$\Delta E_{\text{VBM}}(\text{A/B}) \simeq F(\text{B}) - F(\text{A}). \quad (2)$$

Indeed, paralleling the efforts to calculate $\Delta E_{\text{VBM}}(\text{A/B})$ directly by modeling the A–B interface^{4,5} [i.e., including the two contributions of Eq. (1) at the same time], many attempts^{6–12} have been made to identify the nature of the characteristic energies F which satisfy Eq. (2). Such are the (i) “electron affinity rule⁶” (F identified with the sum of the electron affinity and the band gap); (ii) the “common anion

rule⁷” (where F is taken as the anion ionization potential, hence for AC and BC, with the common anion C one has $\Delta E_{\text{VBM}}^b \simeq 0$); (iii) Harrison's tight binding model⁸; (iv) Van Vechten's dielectric model⁹; (v) the Frensey–Kroemer model¹⁰ (where F is taken as the average electrostatic potential at the tetrahedral interstitial sites); (vi) Zunger's model¹¹ (where F is taken as the donor or acceptor energy of a cation-site transition metal impurity used to probe the valence band offset), and (vii) Tersoff's model¹² (in which the “neutrality level” F is calculated as the energy at which conduction and valence bands contribute equally to an approximate host crystal Green's function). Only models (i), (ii), and (vi) identify F with a directly measurable quantity, and only models (vi) and (vii) predict ΔE_{VBM} for common-anion systems to within the error limits of the underlying linear representation of the data.

The failure of the simple models [(ii), (iii), and (iv) above] in passing the crucial common-anion test was recently interpreted^{12,13} to reflect the neglect^{6–11} of $\Delta E_{\text{VBM}}^{\text{is}}$ —in particular, interfacial charge transfer effects—rather than being due to an imperfect representation by previous calculations^{8,9} of ΔE_{VBM}^b itself. This interpretation^{12,13} grants a decisive physical role to interfacial dipoles in establishing ΔE_{VBM} . There are, however, reason to believe that the opposite is true: since ΔE_{VBM}^b of common-anion lattice-matched pairs (e.g., CdTe–HgTe, GaAs–AlAs) reflects solely the effect of *cation orbitals* on the VBM, simplified band structure models^{8,9} (neglecting, e.g., cation *d* orbitals altogether¹⁴ and using a minimal valence-only basis set for other orbitals) could have misrepresented this quantity.

In this paper we address this problem by calculating ΔE_{VBM} in a way that directly parallels its measurement in photoemission experiments¹⁵—by computing the core level energies. Using a first-principles all-electron band structure model we find that our calculated ΔE_{VBM} values for the two crucial common-anion systems HgTe–CdTe and GaAs–AlAs agree well with recent experimental data. We argue further, using a simple electrostatic model, that $\Delta E_{\text{VBM}}^{\text{is}}$ is small, hence, $\Delta E_{\text{VBM}} \simeq \Delta E_{\text{VBM}}^b$. This suggests that interface-specific dipole contributions to the band offsets are small in these systems.

II. CORE LEVELS AND VALENCE BAND OFFSETS

Figures 1(a) and 1(b) depict schematically the energy level diagram for an AC-BC system. We will denote by E the "binding energies," measured with respect to the VBM (these are most commonly reported both in experimental and theoretical work), and by ϵ the core binding energies with respect to a *material-independent reference* (say, the internal vacuum level, or any other fixed point), common to AC, BC, and their interface. We will treat two (complementary) approaches for establishing ΔE_{VBM} in the system AC-BC: (A) using the levels of the common atom C [Fig. 1(a)], and (B) using the levels of the dissimilar atoms A and B [Fig. 1(b)]. We shall discuss the evaluation of ΔE_{VBM} both with and without interface dipole effects.

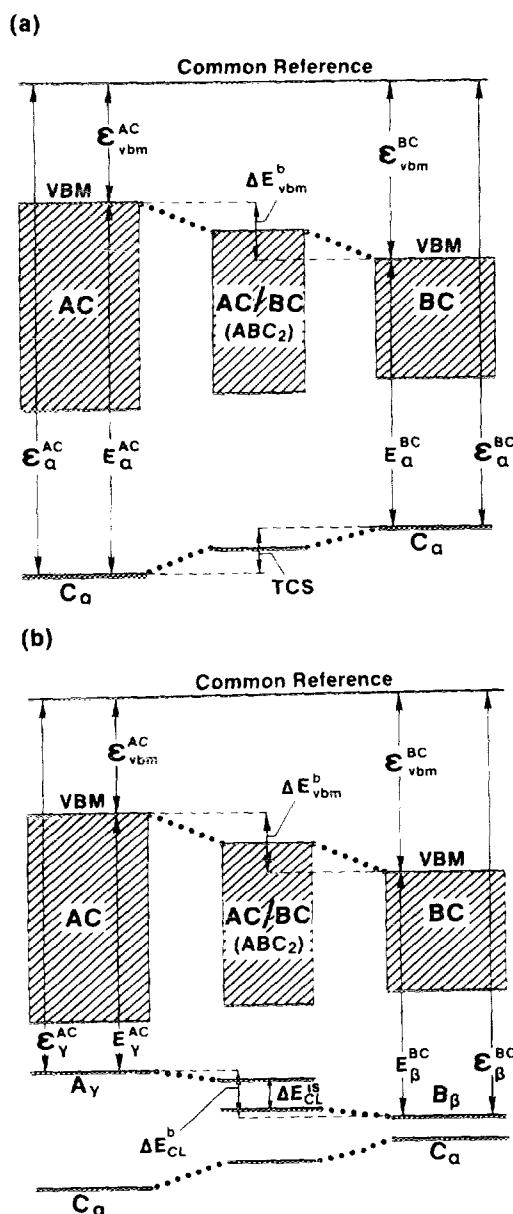


FIG. 1. Schematic plot of energy levels of (a) core level α when the common atom C is used as reference level and (b) core level γ of the A and β of B when A and B are used as reference levels. For details of the symbols used in this plot see the text.

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A. Using the core levels α of the common atom C [Fig. 1(a)]

Since (by Fig. 1), $\epsilon_{\alpha}^{\text{AC}} = E_{\alpha}^{\text{AC}} + \epsilon_{\text{VBM}}^{\text{AC}}$ and $\epsilon_{\alpha}^{\text{BC}} = E_{\alpha}^{\text{BC}} + \epsilon_{\text{VBM}}^{\text{BC}}$ [where, for example, $\epsilon_{\text{VBM}}^{\text{AC}}$ is the separation between the VBM of AC relative to the reference energy, see Fig. 1(a)], the bulk valence band offset $\epsilon_{\text{VBM}}^{\text{AC}} - \epsilon_{\text{VBM}}^{\text{BC}}$ is given by

$$\Delta E_{\text{VBM}}^b(\text{A/B}) = (E_{\alpha}^{\text{BC}} - E_{\alpha}^{\text{AC}}) - (\epsilon_{\alpha}^{\text{BC}} - \epsilon_{\alpha}^{\text{AC}}), \quad (3)$$

where negative $\Delta E_{\text{VBM}}^b(\text{A/B})$ indicates that the VBM of BC is lower than that of AC. The first term in parentheses in Eq. (3) is denoted the "apparent chemical shift" (ACS) of a core level α in BC relative to that in AC, whereas the second term is denoted the "true chemical shift" (TCS). Only the TCS reflects a genuine "chemical" shift due to the changed environment (e.g., charge redistribution) around C in different systems; in contrast, the ACS is not interpretable in terms of charge redistribution alone, since it involves, as in Eq. (3), also the valence band offset.

B. Using the core levels γ of A and β of B [Fig. 1(b)]

An alternative to the above scheme is to use core levels from different atoms A and B as a reference. In such a case the bulk valence band offset is given by [Fig. 1(b)],

$$\Delta E_{\text{VBM}}^b(\text{A/B}) = (E_{\beta}^{\text{BC}} - E_{\gamma}^{\text{AC}}) - (\epsilon_{\beta}^{\text{BC}} - \epsilon_{\gamma}^{\text{AC}}). \quad (4a)$$

In either case [Eqs. (3) or (4)], the calculated (or measured) ACS $E_{\alpha}^{\text{BC}} - E_{\alpha}^{\text{AC}}$ of Eq. (3) or the "apparent core level (CL) difference" $E_{\beta}^{\text{BC}} - E_{\gamma}^{\text{AC}}$ of Eq. (4) are to be corrected by the TCS in case A or by $\Delta E_{\text{CL}}^b = \epsilon_{\beta}^{\text{BC}} - \epsilon_{\gamma}^{\text{AC}}$ in case B (see Fig. 1) for core states belonging to *different* isolated compounds.

In photoemission experiments¹⁵ ΔE_{VBM} was determined in a way similar to method B, measuring the core level binding energies E_{γ}^{AC} and E_{β}^{BC} for the *separate compounds* AC and BC, respectively, whereas the difference ΔE_{CL}^b in Eq. (4a) is replaced by $\Delta E_{\text{CL}}^{\text{is}}$ (see Fig. 1), and measured at the AC-BC interface, that is

$$\Delta E_{\text{VBM}}(\text{A/B}) = (E_{\beta}^{\text{BC}} - E_{\gamma}^{\text{AC}}) - \Delta E_{\text{CL}}^{\text{is}}. \quad (4b)$$

All the interface induced effects are taken to be included in $\Delta E_{\text{CL}}^{\text{is}}$.

C. Charge transfer effects

The TCS between AC and BC can be modeled electrostatically¹⁶ by noting that the existence of an excess electronic charge ΔQ_C in a radius R_{eff} around atom C in compound BC relative to AC results in two opposing effects on the core level energies of C: they move to *lower* binding energies (resulting in shallower levels) by the amount $\Delta Q_C / R_{\text{eff}}$ due to interelectronic repulsion, but the existence of a deeper Madelung potential $-\Delta Q_C \tilde{\alpha} / d$ at this site (where $\tilde{\alpha}$ and d are the Madelung constant and the anion-cation bond length, respectively), *increases* the binding energy (resulting in deeper levels). Hence, for the level α of the common atom C

$$\epsilon_{\alpha}^{\text{BC}} - \epsilon_{\alpha}^{\text{AC}} \approx \frac{\Delta Q_C}{R_{\text{eff}}} \left(1 - \frac{\tilde{\alpha} R_{\text{eff}}}{d} \right). \quad (5)$$

This form, used in the past¹⁶ to calculate the TCS in a number of zinc-blende semiconductors, suggests that for a sufficiently deep (hence, unhybridized) level α the TCS manifests a compensation (perfect when $R_{\text{eff}} = d/\bar{\alpha}$) between two opposing terms. Although the resulting TCS is therefore small, it can, however, be significant on the scale of ΔE_{VBM} . The TCS can be either *positive* (e.g., in most common anion systems, hence the ACS alone *overestimates* ΔE_{VBM}^b), or *negative* (e.g., in most common cation systems, in which case the ACS *underestimates* ΔE_{VBM}^b).

III. RESULTS

A. The apparent chemical shift

We have focused on the common anion systems (although this approach can be extended to include common cation systems if larger superlattices are used, see below). To calculate the ACS [first bracketed term in Eqs. (3)] for Te compounds (ZnTe, CdTe, and HgTe) and As compounds (GaAs and AlAs) we perform semirelativistic general potential linearized augmented plane wave¹⁷ (LAPW) calculations for the respective compounds. Table I shows that for all Te core levels (n,l) ranging from (n,l) = 1s to (n,l) = 4d, the apparent chemical shift $E_{\text{Te},(n,l)}^{\text{AC}} - E_{\text{Te},(n,l)}^{\text{BC}}$ [first term of Eq. (3)] is nearly (n,l) independent (within ± 0.02 eV), suggesting that the Te charges differ only outside the respective core radii.

B. The core level difference and the true chemical shift

The core level difference at the interface $E_{\text{CL}}^{\text{is}}$ is calculated by modeling the interface by an ABC_2 compound in the ordered CuAu-I like structure¹⁸ [space group D_{2d}^5 , identical to an alternating monolayer superlattice in the (001) orientation]. All structural parameters of the ternary compounds¹⁸ are relaxed to attain the minimum total energy. Here we have assumed $\Delta E_{\text{CL}}^{\text{is}}$ is independent of the thickness of the superlattice for these systems. This assumption is justified theoretically (see the Appendix) and experimentally¹⁹ and reflects the fact that interface induced effects are small and

TABLE I. Tellurium and arsenic apparent chemical shifts (ACS), in eV, for common-anion semiconductor pairs. The binding energy (relative to VBM) of the compound to the right-hand side of each pair is larger than the other. Observe that the core ACS depends very weakly on the core level used.

Core level	CdTe/ZnTe	CdTe/HgTe	ZnTe/HgTe	AlAs/GaAs
Te/As, 1s	0.203	0.671	0.468	0.836
Te/As, 2s	0.209	0.660	0.451	0.809
Te/As, 2p	0.208	0.656	0.448	0.812
Te/As, 3s	0.207	0.652	0.445	0.838
Te/As, 3p	0.207	0.653	0.446	0.840
Te/As, 3d	0.208	0.652	0.444	0.839
Te, 4s	0.206	0.648	0.442	...
Te, 4p	0.206	0.648	0.442	...
Te, 4d	0.212	0.644	0.432	...
Average	0.208	0.658	0.450	0.825
	± 0.005	± 0.014	± 0.018	± 0.016

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localized near the interface in common anion systems.

The calculation of the core level difference ΔE_{CL}^b [second bracketed term in Eq. (4a)], or the TCS [second term in Eq. (3)] is more subtle, since band structure calculations of solids in which lattice sums of periodic (infinite) interactions are included do not provide a natural, system-invariant energy level to which all energies can be referred. We found,^{2,11,18} however, that for *lattice-matched common-anion systems the cation core levels are nearly fixed with respect to vacuum in the alloying (or interface-formation) process*. We demonstrate this analytically in the Appendix, where numerical examples (using data from band structure calculations) are also shown. Shih *et al.*¹⁹ have indeed shown previously that if one assumes a vanishing TCS for cations, the difference in measured ACS corresponds closely to the independently measured band offsets. Neglecting these small chemical shifts of cation core states in forming ABC_2 compound [i.e., taking $\Delta E_{\text{CL}}^b \simeq \Delta E_{\text{CL}}^{\text{is}}$ in Fig. 1(b)], we can now calculate the TCS of the anions in Eq. (3) by assuming that the difference between anion and cation core levels in AC ($\epsilon_{\alpha}^{\text{AC}} - \epsilon_{\gamma}^{\text{AC}}$) relative to ABC_2 ($\epsilon_{\alpha}^{\text{ABC}_2} - \epsilon_{\gamma}^{\text{ABC}_2}$) reflects solely the anion TCS ($\epsilon_{\alpha}^{\text{AC}} - \epsilon_{\alpha}^{\text{ABC}_2}$). A similar assumption is made for BC relative to ABC_2 . The TCS between C in AC and in BC [second term in Eq. (3)] is then calculated as

$$\epsilon_{\alpha,C}^{\text{BC}} - \epsilon_{\alpha,C}^{\text{AC}} = (E_{\alpha,C}^{\text{BC}} - E_{\beta,B}^{\text{BC}}) - (E_{\alpha,C}^{\text{AC}} - E_{\gamma,A}^{\text{AC}}) + (E_{\beta,B}^{\text{ABC}_2} - E_{\gamma,A}^{\text{ABC}_2}), \quad (6)$$

where $\epsilon_{\alpha,C}^{\text{BC}}$, for example, means the α th core level of atom C in BC. The advantage of the form of Eq. (6) is that only energy differences of core levels in the same compound are involved, hence a common reference is used. Furthermore, errors in the local density model, as well as core-hole relaxation effects (neglected in our band model) are systematically canceled out since differences in energies *for the same atom* in different environments (binary versus ternary) are used [see Eqs. (3) and (4)]. Table II gives the TCS of the common anion 1s level. The remarkable result is that *the values computed from various choices of cation core levels as reference are constant to within ± 0.02 eV*. Note that this is so only if sufficiently deep (i.e., unhybridized) levels are used as reference in the calculation: the outermost cation d levels are not well suited to this purpose since dispersion and hybridization with anion (and cation, in ABC_2) orbitals which exist at the same energy range obscure the TCS (by at least 50 meV).

We test independently our assumption that $\Delta E_{\text{CL}}^{\text{is}}$ is independent of the thickness of the supercell (and alloy formation) by comparing the TCS of anion calculated from A_3BC_4 and AB_3C_4 with that calculated from ABC_2 . We find for the CdTe–HgTe pair that anion TCS calculated from AB_3C_4 and A_3BC_4 are 0.278 eV and 0.263 eV, respectively (with $A = \text{Cd}$, $B = \text{Hg}$), within 0.03 eV of the one listed in Table II. The transitivity is tested by comparing the value of the TCS for the ZnTe–HgTe pair obtained from Eq. (6) to that obtained from the TCS values of the ZnTe–CdTe and CdTe–HgTe pairs. We find the nontransitivity difference to be < 0.02 eV.

TABLE II. True chemical shifts (TCS), in eV, of the anion 1s level in different semiconductor pairs, using various cation core levels as reference. The common core level of the compound to the right-hand side of each pair is deeper than the other. Observe that the TCS depends very weakly on the core level used.

Cation reference levels	CdTe/ZnTe	CdTe/HgTe	ZnTe/HgTe	AlAs/GaAs
	A = Cd, B = Zn	A = Cd, B = Hg	A = Zn, B = Hg	A = Al, B = Ga
A 1s-B 1s	0.078	0.294	0.191	0.423
A 2s-B 2s	0.080	0.283	0.165	0.408
A 2p-B 2p	0.079	0.284	0.165	0.411
A 3s-B 3s	0.095	0.271	0.152	
A 3p-B 3p	0.094	0.271	0.157	
Average	0.087	0.283	0.172	0.416
	± 0.009	± 0.011	± 0.020	± 0.007

C. The valence band offsets

Using our common anion ACS of Table I and the TCS of Table II, we use Eq. (3) to calculate the $\Delta E_{\text{VBM}}^b \approx \Delta E_{\text{VBM}}$ values depicted in Table III (both with and without the spin-orbit correction²⁰). We estimate that the overall accuracy of our result is about 0.1 eV or better for lattice-matched systems; (the error could be larger for lattice mismatched systems, since in this case the cation-cation distance is changed in ternary compounds relative to the binaries). A direct comparison with experiment also depends on how the lattice mismatch is accommodated (i.e., in a pseudomorphic manner or through misfit dislocations⁴). Our results for the lattice-matched pairs agree very well with recently measured ΔE_{VBM} values for HgTe-CdTe¹⁵ and for AlAs-GaAs.²¹ Since for the remaining two systems (CdTe-ZnTe and ZnTe-HgTe) our results differ substantially from those of Tersoff (by a factor of 10 and $\frac{1}{2}$, respectively, see Table III), measurements could shed light on the validity of these approaches.

IV. CONCLUSIONS: CONTRIBUTION OF CATION *d* ORBITALS TO ΔE_{VBM}

Since the difference between the cations A and B is the only factor distinguishing any two lattice-matched com-

mon-anion semiconductor pairs AC and BC, the substantial $\Delta E_{\text{VBM}} \approx \Delta E_{\text{VBM}}^b$ values obtained in Table III for such systems (HgTe-CdTe and GaAs-AlAs) must necessarily reflect the substantial participation of *cation* orbitals in the valence band maxima. The fact that our approach correctly accounts for the large ΔE_{VBM} of these systems hence suggests that the failure of previous models⁸⁻¹⁰ does not result primarily from the neglect of interfacial charge transfer effects but rather from their imperfect description of the cation orbital content of the VBM.^{14,22} Furthermore, the substantial agreement we find with experiment for the lattice-matched pairs and our simple electrostatic model analysis (see the Appendix) suggest that the *bulk* ΔE_{VBM}^b alone is sufficient to explain the experimentally observed data and interface dipole terms are small in these systems.

We have recently shown²³ that inclusion of occupied cation outermost *d* orbitals leads to an upwards shift of the VBM (in inverse proportion to the disparity between the anion *p* and cation *d* orbital energies). The *difference* in these shifts between two semiconductors hence constitutes a net contribution to ΔE_{VBM} and accounts for most of the discrepancy between previous tight-binding results (Table III) and experiment. This is demonstrated as follows: In tetrahedral symmetry the anion *p* states and cation *d* states both have the

TABLE III. Calculated and observed valence band offsets (in eV), of common-anion semiconductor pairs. The compound to the right-hand side of each pair has the higher VBM. Results are given both with and without the spin-orbit (S-O) correction (Ref. 20). Comparison is given with the tight-binding (Ref. 22) (TB) and Tersoff's (Ref. 12) results.

	CdTe/ZnTe	CdTe/HgTe	ZnTe/HgTe	AlAs/GaAs
ΔE_{VBM} (no S-O)	0.12 ± 0.02^a	0.38 ± 0.03^a	0.28 ± 0.04^a	0.41 ± 0.03^a
ΔE_{VBM} (with S-O)	0.13 ± 0.02^a	0.36 ± 0.03^a	0.25 ± 0.04^a	0.42 ± 0.03^a
Exptl.	...	0.35 ± 0.06^b	...	0.45 ± 0.05^c
ΔE_{VBM}^b (TB) ^d	-0.07	0.00	0.07	0.01
$\Delta E_{\text{VBM}}^{is}$ (TB) ^d	0.00	0.09	0.09	0.15
Tersoff	0.01 ^e	0.51 ^e	0.50 ^e	0.55 ^e

^a Present study.

^b Reference 15.

^c Reference 21.

^d Reference 22.

^e Reference 12.

Γ_{15} representation. Since these two states are not very far from each other in energy [$(\epsilon_{15d} - \epsilon_{\text{VBM}})$ are 7.3, 8.4, and 7.4 eV, for ZnTe, CdTe, and HgTe, respectively, in our band structure calculations], they can couple to each other and produce a significant pd repulsion energy ΔE_{pd} at the VBM. We have estimated the pd repulsion energy ΔE_{pd} using a restricted basis function method (i.e., calculate the shift in cation Γ_{15d} band energy upon removing anion p orbitals from the basis) as well as from the tight-binding method.²³ We find the pd repulsion energy difference $\delta_{pd} = \Delta E_{pd}^{\text{BC}} - \Delta E_{pd}^{\text{AC}}$ are 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. The larger δ_{pd} for pairs with HgC^{VI} compounds is due to the lower binding energy of Hg $5d$ orbitals (and its delocalized character) relative to those of Zn $3d$ and Cd $4d$. The larger δ_{pd} for pairs with AlC^V compound is due to the fact that the *unoccupied* Al $3d$ orbitals are *above* the anion p states, thereby producing a negative ΔE_{pd} . For all the other common anion systems ΔE_{pd} are quite similar so the tight binding model is expected to work reasonably well for these systems.

We conclude that whereas interface charge transfer (“dipole”) effects (which certainly exist) have but a small effect on band offsets in these systems, the true deciding factor are bulk effects the participation of cation d orbitals in the VBM.

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APPENDIX A: ELECTROSTATIC MODEL FOR CORE SHIFTS IN COMMON-ANION SEMICONDUCTORS

We aim to model the *change* $\Delta\bar{V}_A$, $\Delta\bar{V}_B$, and $\Delta\bar{V}_C$ in the orbital energies of the deep core states of atoms A, B, and C, respectively, in the binary zinc-blende (ZB) compounds AC and BC relative to the corresponding core states in the ternary compound ABC₂. We consider, for simplicity, the case of isovalent, lattice-matched binary compounds AC and BC (e.g., GaAs and AlAs, or HgTe and CdTe), i.e., where the nearest-neighbor anion-cation distances are nearly equal: $R_{AC} \cong R_{BC} \equiv d$. We model the ternary ABC₂ system in the CuAu-I-like structure [space group D_{2d}^5 , identical to a (001) monolayer superlattice of AC and BC].

We calculate the TCS of core levels in binary relative to ternary systems by modeling the change in the electrostatic potentials on the cation site A (denoted $\Delta\bar{V}_A$) and the change on the anion site C (denoted $\Delta\bar{V}_C$) upon replacing in A₂C₂ one of the cations (A) by another (B), forming thereby the ternary system ABC₂. We will assume spherical non-overlapping charge distributions around the various atomic sites. As recognized by Shevchik *et al.*,¹⁶ the existence of an excess electronic charge Δq_α in a radius R_α around atom α in one compound relative to the other results in two opposing effects on the core levels of atom α . First, they move to lower binding energies by the amount $\Delta U_\alpha = \Delta q_\alpha / R_\alpha$ due

to interelectronic repulsions, and second, the existence of a deeper Madelung potential at this site *increases* the binding energy by ΔV_α . We will treat these two contributions separately in parts B and C below.

A. Definitions

Assign the net charge q_A^{AC} and q_C^{AC} to sites A and C, respectively, in the binary compound AC. By electroneutrality $q_A^{\text{AC}} = -q_C^{\text{AC}}$. Similarly, assign charges q_B^{BC} and q_C^{BC} to sites B and C, respectively in BC, where electroneutrality requires again $q_B^{\text{BC}} = -q_C^{\text{BC}}$. Define the *disparity* Δq between the cation charges in the binary systems AC and BC as

$$\Delta q \equiv (q_B^{\text{BC}} - q_A^{\text{AC}})/2 \equiv -(q_C^{\text{BC}} - q_C^{\text{AC}})/2. \quad (\text{A1})$$

For the ternary compound ABC₂, assign charges q_A^{ABC} , q_B^{ABC} , and q_C^{ABC} to atoms A, B, and C, respectively, where electroneutrality requires $q_A^{\text{ABC}} + q_B^{\text{ABC}} = -2q_C^{\text{ABC}}$. Define the *disparity* ΔQ between the cation charges in the ternary phase ABC₂ as

$$\Delta Q \equiv (q_B^{\text{ABC}} - q_A^{\text{ABC}})/2. \quad (\text{A2})$$

We may hence think of the *charge rearrangement* ϵ on site A in AC relative to the same site in ABC₂ (or that on site B in BC relative to the same site in ABC₂) as

$$\begin{aligned} q_A^{\text{AC}} &= q_A^{\text{ABC}} - \epsilon, \\ q_B^{\text{BC}} &= q_B^{\text{ABC}} + \epsilon. \end{aligned} \quad (\text{A3})$$

From Eqs. (A1) and (A2), it is easy to see that the charge rearrangement is simply

$$\epsilon \equiv \Delta q - \Delta Q. \quad (\text{A4})$$

Similarly, the charge rearrangement δ on the anion

$$\begin{aligned} q_C^{\text{AC}} &= q_C^{\text{ABC}} + \delta, \\ q_C^{\text{BC}} &= q_C^{\text{ABC}} - \delta \end{aligned} \quad (\text{A5})$$

is readily verified from Eq. (A1) to be

$$\delta \equiv \Delta q. \quad (\text{A6})$$

We will consider the general case where the charge rearrangement $\epsilon = \Delta q - \Delta Q$ on the *cations*, and that (Δq) on the anion are both nonzero and different. Actual self-consistent band structure calculations are able to estimate Δq and ΔQ (see below). In Eqs. (A3) and (A5) we have implied that charges on the cation (anion) sublattice are conserved in the ternary compound (i.e., $2q_C^{\text{ABC}} \simeq q_C^{\text{AC}} + q_C^{\text{BC}}$). This is found to be a good approximation to our self-consistent calculations. From Eqs. (A3)–(A6) we hence have

$$\begin{aligned} q_A^{\text{AC}} &= q_A^{\text{ABC}} - (\Delta q - \Delta Q), \\ q_B^{\text{BC}} &= q_B^{\text{ABC}} + (\Delta q - \Delta Q), \\ q_C^{\text{AC}} &= q_C^{\text{ABC}} + \Delta q, \\ q_C^{\text{BC}} &= q_C^{\text{ABC}} - \Delta q, \end{aligned} \quad (\text{A7})$$

where Δq and ΔQ are given by Eqs. (A1) and (A2), respectively.

We will now model the change in electrostatic potential between AC and ABC₂ (or BC and ABC₂) resulting from the charge rearrangements indicated in Eq. (A7).

B. Change in intersite Madelung potentials

The electrostatic Madelung (M) energy per unit cell can be separated into contributions on different sites, e.g., for AC we have

$$E_M^{AC} = \frac{1}{2} (V_A^{AC} q_A^{AC} + V_C^{AC} q_C^{AC}), \quad (\text{A8a})$$

whereas for ABC_2 we have

$$E_M^{ABC} = \frac{1}{2} (V_A^{ABC} q_A^{ABC} + V_B^{ABC} q_B^{ABC} + 2V_C^{ABC} q_C^{ABC}). \quad (\text{A8b})$$

We wish to calculate first the difference

$$\begin{aligned} \Delta V_A &= V_A^{ABC} - V_A^{AC}, \\ \Delta V_C &= V_C^{ABC} - V_C^{AC} \end{aligned} \quad (\text{A9})$$

due to the intersite Madelung potentials. For the zinc-blende (ZB) structure we have:

$$E_M^{AC} = -\alpha_{ZB} (q_A^{AC})^2 / d, \quad (\text{A10})$$

where α_{ZB} is the Madelung constant for the ZB structure ($\alpha_{ZB} = 1.638$). Using Eq. (A8a) we then have

$$\begin{aligned} V_A^{AC} &= -\alpha_{ZB} q_A^{AC} / d = \alpha_{ZB} q_C^{AC} / d \\ V_C^{AC} &= -\alpha_{ZB} q_C^{AC} / d. \end{aligned} \quad (\text{A11})$$

For the ABC_2 compound in the CuAu-I ($L1_0$) structure we have¹⁸

$$E_M^{ABC} = \frac{-1}{d} \left[2\alpha_{ZB} (q_C^{ABC})^2 + \frac{\sqrt{6}}{4} \alpha_{AB} \Delta Q^2 \right], \quad (\text{A12})$$

where $\alpha_{AB} = 1.594$ is the Madelung constant for the cubic CuAu-I structure. We will denote $\alpha^* = \sqrt{6}\alpha_{AB}/4 = 0.976$ as the effective Madelung constant for the cation (A-B) sublattice in this ABC_2 structure. Equation (A12) can be separated into site contributions as in Eq. (A8b) by using the definitions of Eqs. (A2)–(A7) and the electroneutrality conditions. This yields:

$$\begin{aligned} V_A^{ABC} &= \frac{1}{d} [\alpha_{ZB} q_C^{ABC} + \alpha^* (q_B^{ABC} + q_C^{ABC})], \\ V_B^{ABC} &= \frac{1}{d} [\alpha_{ZB} q_C^{ABC} + \alpha^* (q_A^{ABC} + q_C^{ABC})], \\ V_C^{ABC} &= -\frac{1}{d} \alpha_{ZB} q_C^{ABC}. \end{aligned} \quad (\text{A13})$$

In deriving Eqs. (A10) and (A13) the same reference level (i.e., $V = 0$ at infinity) is used. To find the differences ΔV_A and ΔV_C of Eq. (A9), we subtract the corresponding terms of Eq. (11) from those of Eq. (A13). This gives

$$\begin{aligned} \Delta V_A &= (-\alpha_{ZB} \Delta q + \alpha^* \Delta Q) / d, \\ \Delta V_C &= \alpha_{ZB} \Delta q / d. \end{aligned} \quad (\text{A14})$$

C. Change in on-site Coulomb potential

In addition to the changes ΔV_A and ΔV_C [Eq. (A14)] due to the Madelung potentials, a charge transfer will also produce an on-site Coulomb change. For the anion site, an extra charge $-\Delta q$ in a radius R_C around C atom will change the potential inside R_C by

$$\Delta U_C = \frac{-\Delta q}{R_C}, \quad (\text{A15})$$

whereas an extra charge ϵ on the cation A (in a radius R_A) changes the potential inside R_A by

$$\Delta U_C = \epsilon / R_A = (\Delta q - \Delta Q) / R_A. \quad (\text{A16})$$

D. The total change in electrostatic potentials

Combining Eqs. (A14)–(A16) one obtains the total change in the cation (A) site electrostatic potential in ABC_2 relative to AC

$$\Delta \bar{V}_A = \frac{\Delta q}{d} \left[\lambda \alpha^* - \alpha_{ZB} + \frac{d}{R_A} (1 - \lambda) \right], \quad (\text{A17})$$

whereas the change in the anion site (C) potential in ABC_2 relative to AC is

$$\Delta \bar{V}_C = \frac{\Delta q}{d} \left(\alpha_{ZB} - \frac{d}{R_C} \right), \quad (\text{A18})$$

where $\lambda = \Delta Q / \Delta q$. Notice that, besides the usual partial cancellation of Madelung (α_{ZB}) and intra-atomic (d/R) effects (present both in $\Delta \bar{V}_A$ and $\Delta \bar{V}_C$), the cation shift $\Delta \bar{V}_A$ contains an extra partial cancellation term ($\lambda \alpha^*$) due to the charge fluctuation on the cation sublattice. This is the key to understanding why cation core shifts can be small, hence, why even a *thin* superlattice ABC_2 suffices for our calculations.

We now estimate the numerical values of the parameters in Eqs. (A17) and (A18). In common anion lattice-matched AC and BC systems (where the A–B electronegativity difference is generally small), one expects both the charge disparity Δq and the binary-to-ternary charge transfer $\Delta q - \Delta Q$ to be small (this is not the case for common cation systems). Indeed, our self-consistent calculations show that the charge differences inside the muffin-tin spheres are $\Delta q = 0.024 e$, $\lambda = 0.86$ for CdTe–HgTe and $\Delta q = 0.043 e$, $\lambda = 0.82$ for AlAs–GaAs. To estimate the charge transfer radii R_A and R_C we note that, in forming 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, $R_A < d/2$. The anion sublattice exhibits instead a symmetry-enforced charge mixing, which also suggests $R_C < d/2$. For $\Delta \bar{V}_A$ the choice of R_A is less essential, since its effect is reduced by a factor of $(1 - \lambda)$, where $\lambda = \Delta Q / \Delta q$ is close to 1. Using experimental bond lengths ($d = 2.80 \text{ \AA}$, for CdTe and HgTe; $d = 2.45 \text{ \AA}$ for AlAs and GaAs) and estimating R_A and R_C as $\sim 0.3d$ we find $\Delta \bar{V}_A$ to be about 0.04 eV, whereas $\Delta \bar{V}_C$ is about 3–10 times larger. Note that both in HgTe–CdTe and in AlAs–GaAs our simple model predicts cation and anion core states to have the same sign of TCS (less binding for HgTe and GaAs when alloyed with CdTe and AlAs, respectively). Since $\Delta \bar{V}_A$ on the *cation* sublattice in common-anion pairs is smaller than the uncertainty in our model calculation we assume that $\Delta \bar{V}_A \approx 0$, i.e., that relative to vacuum, deep cation core levels are unchanged in going from the binary compounds AC and BC to the ternary (common-anion) system ABC_2 . This implies $\Delta E_{VBM} \approx \Delta E_{VBM}^b$. Note that if $\Delta \bar{V}_A \approx 0$ as found here, the results obtained in this paper for the band

offset are strictly independent on the superlattice thickness. We hence expect to find the same band offsets using thicker $(\text{AlAs})_n$, $(\text{GaAs})_n$ superlattices. [Massidda, Min, and Freeman (private communication), inform us that the results obtained using $n = 2$ and $n = 3$ are indeed equal to within 0.03 eV. Our analysis of this Appendix explains this finding in term of Eqs. (A17) and (A18)].

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