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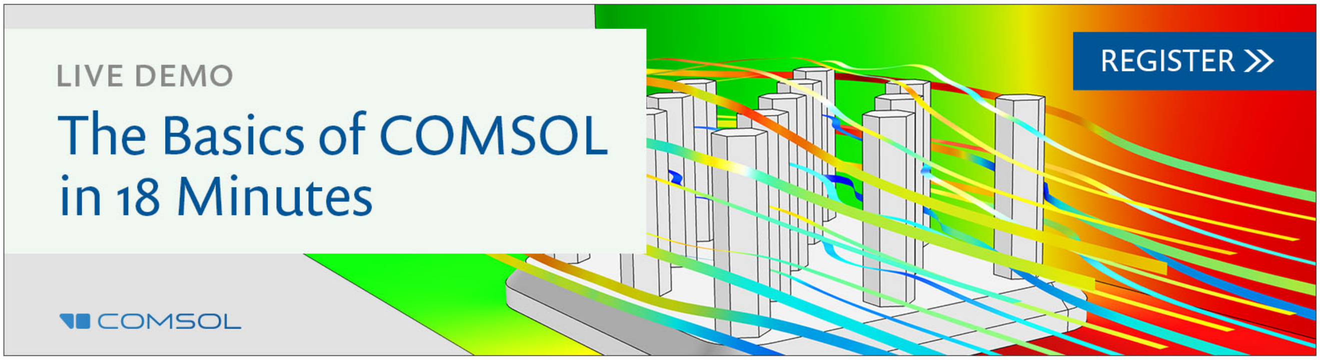

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Calculated natural band offsets of all II–VI and III–V semiconductors: Chemical trends and the role of cation *d* orbitals

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Using first-principles all-electron band structure method, we have systematically calculated the natural band offsets ΔE_v between all II–VI and separately between III–V semiconductor compounds. Fundamental regularities are uncovered: for common-cation systems ΔE_v decreases when the cation atomic number increases, while for common-anion systems ΔE_v decreases when the anion atomic number increases. We find that coupling between anion *p* and cation *d* states plays a decisive role in determining the absolute position of the valence band maximum and thus the observed chemical trends. © *1998 American Institute of Physics.* [S0003-6951(98)03316-6]

The offset $\Delta E_v(AX/BY)$ between the valence (v) band maxima of two semiconductor compounds AX and BY forming a heterostructure is one of the most important parameters in interfacial structures deciding both transport and quantum confinement. Extensive studies (see review in Ref. 1) have been carried out in the past to both measure and calculate ΔE_v of II–VI and III–V semiconductor compounds. However, most of the experimental studies concerned only a particular pair and their results are somewhat scattered. Furthermore, many of the previous theoretical calculations involved approximations (e.g., model solid,[2] no $p-d$ coupling,[3] etc.) whose validity has not been verified. Thus, overall regularities and trends were not apparent. In this letter we have systematically calculated the natural band offsets ΔE_v via *ab initio*, all-electron band structure method[4] between all II–VI and III–V semiconductor compounds. Clear chemical trends are apparent.

To calculate the valence band offset $\Delta E_v(AX/BY)$ between two compounds AX and BY we follow the procedure used in photoemission core level spectroscopy,[5] where the band offset is given by

$$\Delta E_v(AX/BY) = \Delta E^{BY}_{v,C'} - \Delta E^{AX}_{v,C} + \Delta E^{AX/BY}_{C,C'} . \tag{1}$$

Here,

$$\Delta E^{AX}_{v,C} = E^{AX}_{v} - E^{AX}_{C} \tag{2}$$

(and similarly for $\Delta E^{BY}_{v,C'}$) are the core level (C) to valence band maximum energy separations for pure AX (and similarly for pure BY), while

$$\Delta E^{AX/BY}_{C,C'} = E^{BY}_{C'} - A^{AX}_{C} \tag{3}$$

is the difference in core level binding energy between AX and BY at the AX/BY heterojunction. To obtain the *unstrained* ‘‘natural’’ offsets, the core-to-valence-band maximum (VBM) one electron energy difference $\Delta E^{AX}_{v,C}$ is calculated for AX (and similarly for BY) at their respective *equilibrium* (experimental) zinc-blende lattice constants.[6,7] The core level difference $\Delta E^{AX/BY}_{C,C'}$ is obtained here from the calculation for the $(AX)_n/(BY)_n$ superlattices with (001) orientation. We find that for most of the systems $n=3$ is sufficient to converge $\Delta E_{C,C'}(AX/BY)$ within 0.02 eV. The error is larger for a system with large lattice mismatch (e.g., GaN/GaAs). The structural parameters of the superlattice are relaxed using the valence force filed (VFF) model[8] and tested with first-principle force and a total energy minimization scheme. We estimate that the total uncertainty in our calculation in most cases is about 0.05 eV. The error could be larger for systems between nitrides and other III–V compounds or between II–VI and III–V systems. Conduction band offsets can be obtained from our calculated valence band offsets by adding the difference of measured gaps.

The band structure calculation is performed using the local density approximation[9,10] (LDA) of the density functional theory as implemented by the general potential, *relativistic*, all electron, linearized augmented plane wave (LAPW) method.[11] We used the Ceperly–Alder exchange correlation potential[9] as parameterized by Perdew and Zunger.[10]

Our directly calculated valence band offsets are summarized in Table I for common-anion systems and Table II for common-cation systems (numbers without parenthesis). Although the form of Eq. (1) does not obviously lend the AX/BY band offset to be expressed as a linear difference between the AX and the BY valence band maximum of the *isolated compounds*

$$\Delta E_v(AX/BY) = E^{BY}_{v} - E^{AX}_{v} , \tag{4}$$

our directly calculated values show that the transitivity rule

$$\Delta E_v(AX/CX) = \Delta E_v(AX/BX) + \Delta E_v(BX/CX) \tag{5}$$

is well satisfied for the *natural* band offsets between III–V compounds and separately between II–VI compounds, indicating that it is indeed a bulk property. This observation of approximate transitivity makes it possible to define from Eq. (4) the valence band maximum energies of *isolated* compounds (e.g., with respect to a given compound) shown in Fig. 1. Transitivity also allows us to derive the band offsets between pairs that have not been calculated directly (numbers in parenthesis in Table I and Table II).

Our calculated results show the following trends:

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TABLE I. Calculated natural valence band offsets $\Delta E_v(AX/BX)=E_v(BX)-E_v(AX)$ between common-anion II–VI and III–V compounds. The numbers in the parenthesis are deduced from the transitivity rule, whereas others are obtained from direct supercell calculations. Energy is in eV.

II–VI systems						
X	Mg/Zn	Zn/Cd	Cd/Hg	Mg/Cd	Mg/Hg	Zn/Hg
S	⋯	(0.18)	(0.66)	⋯	⋯	(0.84)
Se	(1.03)	(0.07)	(0.47)	(1.10)	(1.57)	(0.54)
Te	(0.76)	−0.13	0.37	(0.67)	1.05	0.26
III–V systems						
	Al/Ga	Ga/In	Al/Tl	Al/In	Al/Tl	Ga/Tl
N	0.84	0.26	⋯	1.04	⋯	⋯
P	0.54	0.11	⋯	0.68	⋯	⋯
As	0.51	0.05	⋯	0.58	⋯	⋯
Sb	0.41	−0.01	⋯	0.43	⋯	⋯

(i) Most valence band offsets are nonzero. This is in contrast with the ‘‘common-anion rule’’[12,13,3] that suggested that the offset between two semiconductors having the same anion will be small. The smallest ΔE_v occur between Zn/Cd and Ga/In common-anion systems (Table I).

(ii) For common-anion pairs, ΔE_v decreases as the atomic number of the anion increases. For example, the offset between tellurides is smaller than that between selenides or between sulphides (Table I). The change is larger in II–VI systems than in III–V systems.

(iii) For common-cation pairs, ΔE_v decreases as the atomic number of the cation increases. For example, the offset between Hg chalcogenides is smaller than that between Cd chalcogenides or between Zn chalcogenides (Table II). Again, the change is larger in II–VI systems than in III–V systems.

(iv) For common-cation pairs, the compound with larger anion atomic number also has a higher VBM energy (Fig. 1), i.e., E_v follows the order of anion *p* orbital energies.

A long-standing paradigm in the theory of zinc-blende semiconductors is that the VBM wave functions are made of anion *p* states with small contributions from cation *p* states. This is clear in the tight binding model of Harrison[14,3] as well as in the model of Vogle, Hjalmarson, and Dow.[15] Since all the cations with the same valence have similar *p* orbital energies, this *p*-VBM view naturally leads to the conclusions that if two semiconductors have the same anion, their valence band offset will be close to zero (the common-anion rule[12,13,3]). Trends (i) and (ii) above show that this expectation is not met. Furthermore, the *p*-VBM model also suggests that the valence band offset for the common-cation systems reflects mostly the *p* orbital energy differences between the two anions, and is thus not sensitive to the identity of cations. This conflicts with trend (iii). Furthermore, the calculated ΔE_v values from the *p*-VBM model[3] are much larger than our calculated values (see below).

We show here that the observed trends above can be understood if $p-d$ coupling[4] in these systems is taken into account. In the zinc-blende compound with T_d site symmetry both the anion *p* and the cation *d* orbitals transform (among others) as the Γ_{15} (also called t_2) representation. These two equal-symmetry states can thus interact with each other. The interaction between the anion *p* and the occupied cation *d* states results in a level repulsion, moving the VBM *upwards* (Fig. 2). The coupling is proportional to the matrix square $V_{\mathrm{pd}}^2=|<X,p|\Delta V|A,d>|^2$ (larger for compounds with more delocalized *d* orbitals and short bond length), and is inversely proportional to the unperturbed energy difference $|\epsilon_p-\epsilon_d|$ (larger for compounds with low anion *p* orbital en-

TABLE II. Calculated natural valence band offsets $\Delta E_v(AX/AY)=E_v(AY)-E_v(AX)$ between common-cation II–VI and III–V compounds (see Table I caption).

II–VI systems						
A	O/S	S/Se	Se/Te	O/Se	O/Te	S/Te
Mg	⋯	⋯	1.00	⋯	⋯	⋯
Zn	1.00	0.53	0.73	(1.53)	(2.26)	1.26
Cd	⋯	0.42	0.57	⋯	⋯	0.99
Hg	⋯	0.23	0.46	⋯	⋯	(0.69)
III–V systems						
	N/P	P/As	As/Sb	N/As	N/Sb	P/Sb
Al	(1.97)	0.54	(0.66)	(2.47)	(3.13)	(1.16)
Ga	1.72	0.43	0.58	2.19	(2.75)	(1.04)
In	(1.56)	(0.42)	0.50	(1.98)	(2.48)	(0.92)

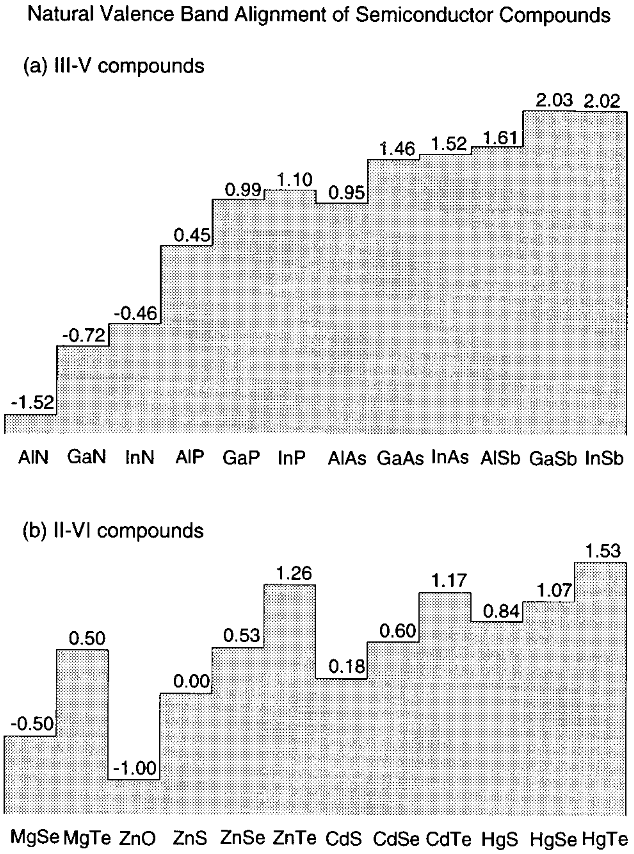

FIG. 1. Calculated natural valence band alignment of (a) III–V semiconductor compounds and (b) II–VI semiconductor compounds.

ergy and higher cation d orbital energy). Figure 2 shows schematically how the $p-d$ coupling affects the band offset:

(a) Trend (i) for common-anion systems is a consequence of the fact that the two cations have different d orbital energies and different spatial extent of the d orbitals. The cation with shallower d bands repels the anion p band upwards more than the cation with deeper d band. This differential effect increases ΔE_v [Fig. 2(a)]. In general, $p-d$ repulsion increases when the cation atomic number increases. For example, the *large* band offsets between common-anion Al/In, Al/Ga, Mg/Zn, Mg/Cd, and Mg/Hg pairs are due to the fact that Al d and Mg d orbitals are unoccupied (higher in energy than the anion p level), while the Ga, In, Zn, Cd, and Hg d orbitals are occupied (lower in energy than the anion p level). The *large* band offsets between the common-anion Zn/Hg and Cd/Hg pairs are due to the fact that the Hg 5d orbital has a shallower energy and is more delocalized than the Cd 4d or Zn 3d orbitals, thus the $p-d$ repulsion is much larger in the Hg compounds. The relatively small band offset between the common-anion Ga/In and Zn/Cd pairs is due to the fact that, although the In and Cd 4d orbitals are more delocalized than the Ga and Zn 3d orbitals, the anion–cation bond lengths in the Ga compounds and in the Zn compounds are shorter than in the In or Cd compounds, respectively.

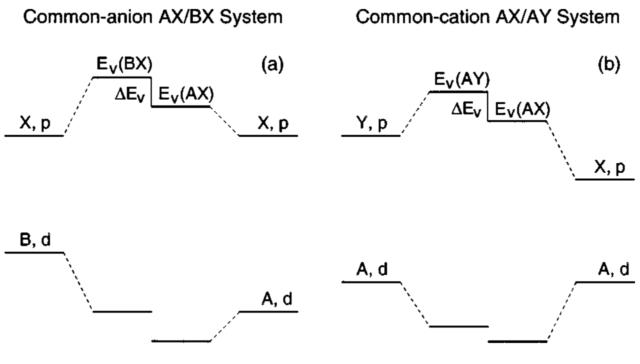

FIG. 2. Schematic plot of $p-d$ repulsion effects on valence band offsets of (a) common-anion AX/BX system and (b) common-cation AX/AY system.

(b) For the common-anion system, without $p-d$ coupling, ΔE_v will be small as expected from the p-VBM model.[3] Since the $p-d$ repulsion decreases as the anion atomic number increases (due to the increase of the anion p orbital energy and increase of the bond lengths), ΔE_v decreases when the anion atomic number increases (e.g., from 0.66 eV for CdS/HgS to 0.47 eV for CdSe/HgSe to 0.37 eV for CdTe/HgTe). This explains trend (ii) above.

(c) For the common-cation system, a compound with smaller atomic number also has a lower VBM energy (as predicted by the p-VBM model[3]). However, since the anion with smaller atomic number also has lower p orbital energy and smaller anion–cation bond length, the upward shift of its VBM energy due to $p-d$ repulsion is larger than the compound with larger anion atomic number. This decreases the ΔE_v. For example, for the ZnS/ZnTe and GaN/GaP pairs, without $p-d$ coupling the ΔE_v are 2.2[3,2] and 4.38 eV,[3] respectively, while with $p-d$ coupling, the ΔE_v is only 1.26 and 1.72 eV, respectively. Since $p-d$ repulsion increases when the cation atomic number increases, ΔE_v is reduced as the atomic number of the cation increases (e.g., from 0.53 eV for ZnS/ZnSe to 0.42 eV for CdS/CdSe to 0.23 eV for HgS/HgSe). This explains trend (iii) above.

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[1] E. Yu and T. McGill, in *Solid State Physics*, edited by H. Ehrenreich and D. Turnbull (Academic, Boston, 1992), Vol. 46, p. 1 and references therein.
[2] C. G. Van de Walle, Phys. Rev. B **39**, 1871 (1989).
[3] W. A. Harrison, J. Vac. Sci. Technol. **14**, 1016 (1977); J. Vac. Sci. Technol. B **3**, 1231 (1985).
[4] S.-H. Wei and A. Zunger, Phys. Rev. Lett. **59**, 144 (1987); Phys. Rev. B **37**, 8958 (1988).
[5] S. P. Kowalczyk, J. T. Cheung, E. A. Kraut, and R. W. Grant, Phys. Rev. Lett. **56**, 1605 (1986); T. M. Duc, C. Hsu, and J. P. Faurie, *ibid.* **58**, 1127 (1987).
[6] *Landolt-Bornstein: Numerical Data and Functional Relationships in Science and Technology*, edited by O. Madelung, M. Schulz, and H. Weiss (Springer, Berlin, 1982), Vol. 17a,b and Vol. 22a.
[7] For compounds that are stable in the wurtzite structure, we assume that the zinc-blende phase has the same volume as the wurtzite phase.
[8] J. L. Martins and A. Zunger, Phys. Rev. B **30**, 6218 (1984).
[9] D. M. Ceperly and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[10] J. P. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).
[11] S.-H. Wei and H. Krakauer, Phys. Rev. Lett. **55**, 1200 (1985), and references therein.
[12] J. O. McCaldin, T. C. McGill, and C. A. Mead, Phys. Rev. Lett. **36**, 56 (1976).
[13] W. R. Frensley and H. Kroemer, Phys. Rev. B **16**, 2642 (1977).
[14] W. A. Harrison, *Electronic Structure and Properties of Solids* (Freeman, San Francisco, 1980), pp. 74–80.
[15] P. Vogle, H. P. Hjalmarson, and J. D. Dow, J. Phys. Chem. Solids **44**, 365 (1983).