

Band Lineups at II-VI Heterojunctions: Failure of the Common-Anion Rule

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Band-edge discontinuities are calculated for tellurium-based II-VI heterojunctions. Contrary to the widely accepted common-anion rule, large valence-band discontinuities are found in most cases, including HgTe-CdTe. The common-anion rule is examined and predicted to fail, not only here, but for all lattice-matched II-VI and III-V heterojunctions. An experiment is proposed to test these predictions.

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II-VI semiconductors and their heterojunctions have attracted wide interest because of their unique electronic properties, which promise new physical effects and novel device applications.¹ In this paper a recent theory of heterojunction band lineups² is extended for the first time to II-VI semiconductors. For the Te-based compounds studied here, large valence-band discontinuities are predicted in almost all cases, in direct contradiction to previous theories³ and to the widely used common-anion rule.^{4,5} In addition, the common-anion rule is critically examined, and is predicted to fail for *all* lattice-matched heterojunctions, including both II-VI's and III-V's.

The band lineup specifies the relative energies of the band edges in the respective semiconductors at the interface. Because of the lack of direct data on II-VI band lineups, substantial reliance has been placed upon the so-called "common-anion rule" in the attempt to interpret experimental results. This rule^{4,5} states that the valence-band discontinuity ΔE_V at the interface will be "very small" for semiconductors with the same anion. However, for the tellurium "common-anion" family treated here, the common-anion rule is predicted to fail for all but the ZnTe-CdTe interface, in close analogy to its recently discovered failure⁶ for AlAs-GaAs.

Until recently,^{2,7} all general theories of heterojunction band lineups were based on the idea that there is no dipole induced when two different semiconductors are joined to form a heterojunction.³ The most successful³ of these theories is the tight-binding approach of Harrison.⁸ In contrast to the results here, that theory gives no valence-band discontinuity greater than 0.2 eV for the tellurides considered here, with a discontinuity of only 0.05 eV for the important HgTe-CdTe interface.⁹

The basic idea behind the present theory^{2,7} is that the semiconductor heterojunction is closely analogous to a metal-metal junction. For that well-understood case, any difference in the work functions (i.e., in the electronegativities) of the two metals results in charge transfer, and hence a dipole, which may be viewed as growing until it is large enough to arrest further charge transfer. This equilibrium occurs when the Fermi levels in the two metals line up. In effect, the discon-

tinuity in the electronegativity is screened by the (infinite) dielectric constant of the metal.

It was argued elsewhere^{2,10,11} that there is an energy associated with each semiconductor which plays a role analogous to E_F in a metal. That energy was called E_B in analogy to the branch point in the complex band structure of a one-dimensional semiconductor, and represents the energy (usually deep in the gap) where the states are nonbonding on the average. Any discontinuity in E_B at the interface amounts to a discontinuity in the electronegativity, which will give rise to a charge-transfer dipole. The net result is that the discontinuity in E_B is screened by the (large) dielectric constant of the semiconductor.² In the limit of large dielectric constant, $\epsilon_\infty \rightarrow \infty$, the self-consistent band lineup should then be given by the alignment of E_B in the respective semiconductors at the interface, just as one aligns E_F at a metal-metal junction.

If E_B is given relative to E_V , then continuity of E_B across the interface implies that

$$\Delta E_V = -\Delta E_B, \quad (1)$$

where Δ refers to differences across the interface. Similarly, at a metal-semiconductor interface, to obtain the (*p* type) Schottky barrier ϕ_{bp} one aligns E_B with E_F in the metal, giving¹⁰

$$\phi_{bp} = E_B. \quad (2)$$

One can apply linear-response theory, following Tejedor and Flores,⁷ to show that the correction to (1) for finite ϵ_∞ is simply

$$\epsilon_\infty^{-1}(\Delta E_B - \Delta\Phi), \quad (3)$$

where Φ is the semiconductor ionization potential. Typically, the magnitude of $\Delta E_B - \Delta\Phi$ is less than^{2,7,8} 0.5 eV, so the correction (3) to (1) is only of order 0.05 eV, and (1) suffices by itself. Similar arguments suggested¹² that the pinning strength for Schottky barriers is directly proportional to ϵ_∞^{-1} , again giving good agreement with experiment.

Since the II-VI semiconductors considered here have slightly smaller ϵ_∞ than III-V's, it is prudent to assume that the accuracy will be slightly less here than for III-V's, perhaps ± 0.2 eV on the average.

A simple method for the calculation of E_B directly from the bulk semiconductor band structure was described elsewhere.^{10,13} This approach, in conjunc-

tion with (1) and (2), appears to give rather accurate predictions of band lineups and Schottky barriers, at least for elemental and III-V semiconductors.^{11,14,15} In brief, the band structure is used to generate a cell-averaged real-space Green's function which describes the gap states at a given energy. The effective gap center E_B is defined as that energy where the gap states take their spectral weight equally from the valence and conduction bands, in analogy to the branch point in the complex band structure in one dimension. The effect of spin-orbit splitting is included approximately.¹³ The effect of strain is neglected here, but may be included in a similar manner.^{13,16} For alloys, E_B can be estimated by linear interpolation from the pure semiconductors.

MnTe alloys are of great interest because of their semimagnetic properties, which allow tunable control of the electronic properties by means of an applied magnetic field. Here the Mn d orbitals are taken as frozen in a paramagnetic atomic $3d^5$ configuration, and not allowed to mix with the valence and conduction bands. This approximation doubtless reduces the accuracy of the MnTe results.

The results are summarized in Fig. 1(a), which shows E_B for four tellurium compounds, as well as for three arsenic compounds. Table I gives numerical results for a number of II-VI and III-V semiconductors. (Many of the III-V results were previously pub-

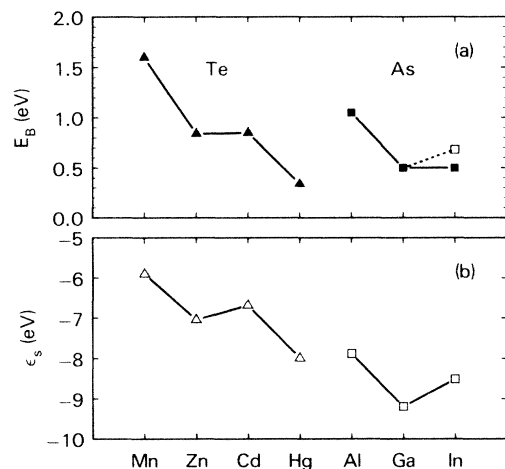


FIG. 1. (a) Calculated values of the effective gap center E_B from Table I for MnTe, ZnTe, CdTe, and HgTe, and for AlAs, GaAs, and InAs, measured from E_V . The valence-band discontinuity at the interface is $\Delta E_V \approx -\Delta E_B$. For InAs, the open square indicates the value obtained for InAs at the GaAs lattice constant, to show the effect of changing the cation while holding the lattice constant fixed. (b) Calculated s eigenvalues for the respective cations, from a Herman-Skillman-type scalar relativistic method. Divalent atoms are taken in an $s^{1.5}p^{0.5}$ configuration. These values are intended primarily as a semiquantitative indication of the atomic pseudopotential.

lished in Ref. 2; others are new, and are provided to complete the respective common-anion families.) Valence-band offsets are given by (1); E_B for alloys may be estimated by linear interpolation. The most striking feature is that the predicted valence-band offsets are quite large, 0.5 eV or more, for all telluride pairs except ZnTe-CdTe.

The HgTe-CdTe interface is of particular interest because of its potential application in infrared detectors.¹⁸ However, some proposed device designs require a very small valence-band discontinuity,¹⁹ as is expected on the basis of the "common-anion rule." Moreover, any analysis of interface electronic properties (e.g., to model device behavior or interpret experimental spectra) requires knowledge of ΔE_V .

Until very recently the only lineup experiment available for an abrupt HgTe-CdTe interface was the magnetoabsorption measurement of Guldner *et al.*²⁰ They reported a valence-band offset of 0.04 eV, based on the good agreement between experiment and theory for that offset. However, their experiment could not rule out a much larger band offset.²¹

Kuech and McCaldin²² measured the Schottky barrier for HgTe (a semimetal) on n -CdTe, but with a very diffuse interface. They obtained an upper bound of 0.5–0.8 eV for ΔE_V , consistent with the present results. However, no lower bound was obtained.

After the present calculations were completed, and the results had been circulated privately, Kowalczyk *et al.*²³ completed the first *direct* measurement of the

TABLE I. Semiconductor "midgap" energy E_B , and measured Fermi-level positions at metal-semiconductor interfaces, relative to valence maxima (in electronvolts).

	E_B	E_F (Au) ^a	E_F (Al) ^a
Si	0.36	0.32	0.40
Ge	0.18	0.07	0.18
AlP	1.27		
GaP	0.81	0.94	1.17
InP	0.76	0.77	
AlAs	1.05	0.96	
GaAs	0.50 ^b	0.52	0.62
InAs	0.50	0.47	
AlSb	0.45	0.55	
GaSb	0.07	0.07	
InSb	0.01	0.00	
ZnSe	1.70	1.34	1.94
MnTe	1.6 ^c		
ZnTe	0.84		
CdTe	0.85	0.73	0.68
HgTe	0.34		

^aReference 17.

^bSee Ref. 13 for this revised value.

^cZinc-blende structure assumed. See text for approximations.

HgTe-CdTe band lineup, using photoemission. While such experiments are notoriously difficult, their result, $\Delta E_V = 0.35 \pm 0.06$ eV, certainly appears to support the present prediction of a large discontinuity $\Delta E_V = 0.5 \pm 0.2$ eV.

While no direct measurements of band offsets exist for ZnTe-CdTe, the offset can be inferred from the empirical table of relative valence-band energies compiled by Margaritondo,^{14,15} expanding the original table of Katnani and Margaritondo. This approach gives a valence-band discontinuity of 0.10 ± 0.15 eV, in good agreement with the present result of -0.01 eV.

Previous results^{2,13} of the present theory for arsenides are included in Fig. 1(a). The predicted drastic failure of the common-anion rule for AlAs-GaAs appears to be well confirmed experimentally,⁶ giving further indirect support for the present conclusions for II-VI's. From Table I, it is evident that other common-anion families are expected to exhibit very similar behavior.

The idea behind the common-anion rule^{4,5} is that the valence-band maximum derives mainly from the anion p states, so that its energy should be relatively independent of the cation. This simple idea is put on a firmer footing in Harrison's tight-binding theory,⁸ where it is seen to be approximately valid, especially for lattice-matched materials, if one assumes that no significant dipole is induced at the interface. As discussed above, the opposite conclusion regarding interface dipoles is drawn here (and more recently by Harrison and Tersoff also⁹) and so the conduction bands and hence the cation are expected to play a crucial role.⁵

If the cation orbital energies are low because of a very attractive cation pseudopotential, then the conduction band is pulled down relative to the valence maximum, and so the effective gap center E_B is lowered. This qualitative effect is illustrated in Fig. 1(b), where the cation atomic s eigenvalues are compared with the calculated values of E_B in Fig. 1(a). The trends are seen to be almost identical. In fact, E_B follow the atom eigenvalues even more closely if the semiconductor lattice constant is held fixed, as indicated by the open square in Fig. 1(a). The lattice expansion upon going from ZnTe to CdTe, or from GaAs to InAs, reduces the gap and hence lowers E_B (or, more precisely, raises E_V relative to E_B), resulting in a fortuitous accuracy for the common-anion rule in those cases.

Note that with increasing atomic number down a column in the periodic table, the atomic size (and hence the semiconductor lattice constant) increases except where there is a change in core symmetry, i.e., p to d for Al-Ga and d to f for Cd-Hg. Lattice-matched common-anion heterojunctions are obtained

only by the crossing of such a boundary. This generally entails a large change in the pseudopotential and hence in the atomic eigenvalues, so that according to the present theory the common-anion rule will apparently *never* be successful for lattice-matched II-VI or III-V heterojunctions. This conclusion is strengthened by the apparent role of lattice expansion in making the common-anion rule fortuitously successful for (Ga,In)As and (Zn,Cd)Te.

The main obstacle to the measurement of band offsets in II-VI heterojunctions is the difficulty of obtaining interfaces of sufficiently high quality. From (1) and (2) one immediately obtains that

$$\Delta E_V \simeq -\Delta\phi_{bp}, \quad (4)$$

i.e., the valence-band discontinuity is given by the difference in measured¹⁷ (p type) Schottky barrier heights for a given metal on the respective semiconductors. This prediction, which is independent of any numerical calculation, has been well verified experimentally.^{11,15} Since Schottky-barrier measurements do not require ideal molecular-beam-epitaxy-grown interfaces, it seems natural that band lineups for these compounds be estimated tentatively from the Schottky-barrier heights, until more direct measurements are possible.

[It is interesting to note that the common-anion rule was in fact first proposed in the context of Schottky barriers.⁴ It was suggested that ϕ_{bp} was approximately independent of the cation for compounds with a given anion. However, the rule was applied only to III-V's whose cation was Ga or In and II-VI's with Cd or Zn, where its success is consistent with Fig. 1(a) and Table I. The rule's failure for Schottky barriers to Al or Hg compounds was evident even at that time.]

For HgTe, which has a negative gap, and for zinc-blende structure MnTe, which occurs only in alloys, one can extrapolate Schottky barriers from alloys with CdTe, etc. For example, the HgTe-CdTe valence-band discontinuity should be given approximately by

$$\Delta E_V \simeq -(d/dx)\phi_{bp}(\text{Hg}_x\text{Cd}_{1-x}\text{Te}), \quad (5)$$

in the range $x < 0.8$ where the alloy is semiconducting. Unfortunately, I know of no existing measurements of the necessary alloy barrier heights. Such Schottky-barrier measurements of II-VI alloys should, I believe, be a high priority in the study of II-VI heterojunction interfaces.

Estimates of band lineups based on measured Schottky-barrier heights will only be accurate to the extent that the semiconductors exhibit strong pinning, so that a careful experiment would use at least two nonreactive metals with very different electronegativities. For each metal, ΔE_V is inferred by use of (4), and the difference in values of ΔE_B obtained with the different metals provides an estimate of the error.

In conclusion, a previous theory for band lineups has been extended to II-VI heterojunctions. The common-anion rule was examined and was predicted to fail for most III-V and II-VI interfaces, including all lattice-matched heterojunctions. In particular, an unexpected large valence-band discontinuity was predicted for HgTe-CdTe, which appears to be confirmed by the recent results of Kowalczyk *et al.*²³

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