VOLUME 59, NUMBER 1 PHYSICAL REVIEW LETTERS 6 JULY 1987 Role of d Orbitals in Valence-Band Offsets of Common-Anion Semiconductors Su-Huai Wei and Alex Zunger
Solar Energy Research Institute,

VOLUME 59, NUMBER 1 PHYSICAL REVIEW LETTERS 6 JULY 1987 TABLE I. Tight-binding, all-electron, and experimental valence-band offsets (in electronvolts)

VOLUME 59, NUMBER 1 PHYSICAL REVIEW LETTERS 6 JULY 1987

AC

AC E,b

gAC gAC
vbm nl, A

ABC2

ABC'
vbm

~BC ~vbm
]I

dEvbm

by all other

VOLUME 59, NUMBER

1 PHYSICAL REVIEW LETTERS

6 JULY 1987

ZnTe-HgTe, AlAs-GaAs, GaAs-InAs, and AlAs-InAs
pairs, respectively. Note that Bpd is large for Hg-
containing semiconductor pairs (since the Hg Sd orbitals are shallower than other column-II cation

d orbitals, and
hence repel the VBM more effectively) and for AI-
containing compounds (since the empty Al 3d orbitals are higher in energy than the anion

p orbitals, and hence
AF~d is negative) Fo.

r all other common-anion pairs
AEpp is similar, and hence the tight-binding model is ex-
pected to work well for these systems.
In conclusion, we find that the principal error in previ-ous tight-binding models for band lineup in lattice-matched compounds (and to a lesser extent also in
plane-wave pseudopotential models which also neglect
occupied cation

d bands) is omission of cation

d orbitals,
and that the assertion that interface dipole eAects 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 photo-emission measurements of the band oAsets in CdTe-

Zn Te (0.10~ 0.06 eV) and Zn Te-Hg Te (0.25 ~ 0.05
eV), in excellent agreement with our independent predic-tions of