

ELECTRONIC STRUCTURE OF II–VI COMPOUNDS AND THEIR ALLOYS – ROLE OF CATION d BANDS

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Traditionally the electronic structure of II–VI compounds was treated theoretically through tight-binding or pseudopotential models, neglecting the cation d bands, despite the fact that they are located less than ~ 10 eV below the valence band maximum (VBM). Applying first-principle all-electron band structure and total energy methods to ZnTe, CdTe, and HgTe and their ordered alloys, we show that inclusion of cation d states on the same footing as other valence states leads to a number of qualitative and quantitative changes in the predicted electronic structure. These include effects on: (i) the predicted band gaps, (ii) the spin–orbit splitting at the VBM, (iii) the band offset between two II–VI compounds, (iv) the cohesive energy, and (v) the direction of charge transfer in an alloy.

1. Introduction

II–VI semiconductor compounds, their alloys, and superlattices have been of great interest in recent years because of the relevance of their electronic properties to applications such as infrared detectors, solar cells, and other devices [1,2]. Efforts to improve material quality in these systems naturally require an understanding of their electronic structure. Traditionally the electronic structure of II–VI compounds was studied theoretically through tight-binding [3,4], empirical [5] and self-consistent [6] pseudopotential methods, neglecting the cation d bands. (Whereas early applications using the KKR [7] or OPW [8] approaches incorporated the cation d bands, surprisingly, more modern attempts [3–6,9–10] have ignored them.) Similarly, studies of II–VI alloys using the virtual crystal approximation [5,10] or the coherent potential approximation [9] have also employed simple electronic structure methods neglecting d bands. Despite the fact that the outermost cation d orbitals are located less than ~ 10 eV below the valence band maximum (VBM), it was hoped [3–6,9–10] that in some sense these orbitals were inactive in the II–VI compounds. In this paper we will show through first principles local density functional (LDF) [11] calculations that neglect of cation d bands is unjustified and

leads to qualitative changes in the properties related to the upper valence and lower conduction bands [12–15].

2. Method of calculation

The all-electron, general potential, linearized augmented plane wave (LAPW) method [16] is used in this study. This approach is particularly suitable for II–VI systems since it uses both localized orbitals (describing well the localized cation d orbitals) and plane waves (describing well the sp orbitals between atoms). Relativistic effects are included. All the valence states (including the outermost cation d states) as well as core states are treated self-consistently. Since this is a first principles calculation the only inputs are the atomic numbers and symmetry information on the crystal structure.

3. Simple physical model

Our objective in this study is to examine how cation d bands affect electronic and structural properties of II–VI systems. Their significance can be qualitatively surmised from the following simple considerations: (i) in II–VI systems the en-

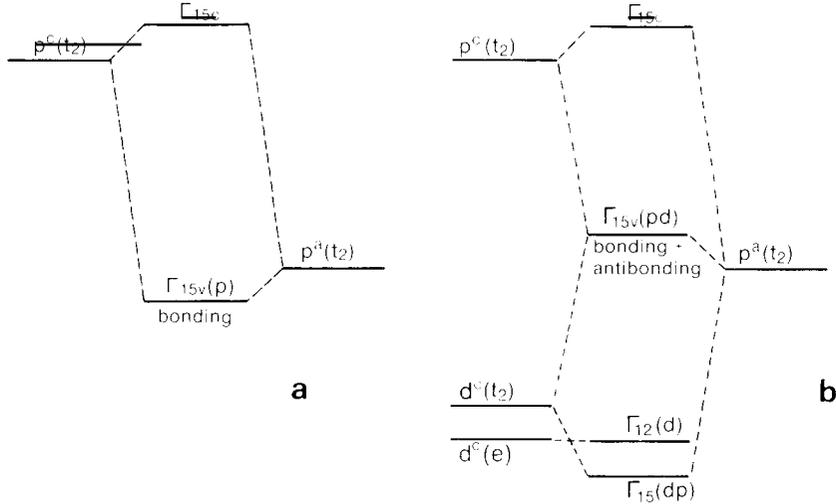


Fig. 1. Schematic plot of p-p and p-d coupling in zincblende semiconductor: (a) p-p coupling only (b) inclusion of p-p and p-d coupling.

ergies of the cation d bands are not too far from the VBM. The calculated energies of the cation-derived d band Γ_{15d} are 7.27, 8.43 and 7.38 eV below the VBM for ZnTe, CdTe, and HgTe, respectively (i.e., a few eV *above* the bottom of the valence band). (ii) In a tetrahedral zincblende crystal the anion p orbitals have the same symmetry representation (t_2 or Γ_{15}) as the cation d orbitals (the other d states with e or Γ_{12} symmetry do not couple with anion p states). Thus p-d hybridization is allowed by symmetry. (iii) The spatial extent (orbital moments) of the outer d orbitals [17] in Zn, Cd, and Hg is 0.913, 1.293 and 1.504 a.u., respectively, i.e., 18.3%, 24.4% and 28.4% of the anion-cation bond length. These indicate that p-d coupling could be quite significant [12–15], since this coupling is inversely proportional to the energy differences and directly proportional to the p-d overlap. We depict these observations in fig. 1. We see that, including only the coupling of cation and anion p states (fig. 1a), the Γ_{15v} valence band maximum is lower in energy than the atomic anion level and that this state is *bonding*. Upon including the p-d hybridization (fig. 1b), however, the Γ_{15v} state is pushed upward in energy, incorporates some d states, and exhibits some *antibonding* character. The Γ_{15d} state is then lower than the Γ_{12d} state due to p-d repulsion. In addition, since the cation d orbitals are fairly

extended, they also directly contribute to ground state properties [13]. Note that whereas previous studies have indirectly incorporated d electron effects by using *atomic* quantities (pseudopotentials [5,6] or orbital energies [3,4]) which exhibit d screening, they all neglected the *d bands*, hence the p-d quantum repulsion effects indicated in fig. 1b.

4. Results

By comparing results obtained from calculations with and without the inclusion of the d orbitals, we observed the following d-orbital induced changes:

(i) Table 1 lists the calculated ground state properties of ZnTe, CdTe, and HgTe as obtained by total energy minimizations. Our results (“with d”) are contrasted with those of Hass and Vanderbilt’s pseudopotential (PS) calculation [6], which omitted the cation d band from the spectrum of valence states (“no d”). Comparison with the experimental value [1,18–22] is also given. We see from table 1 that the results which include the cation d bands, are in reasonable agreement with experiment. In contrast, in the pseudopotential calculation [6] an ad hoc repulsive potential had to be added to correct the errors caused by omission

Table 1

Comparison of calculated ground state properties (with d) of ZnTe, CdTe and HgTe with pseudopotential results (no p-d repulsion or “no d”) of ref. [6], and experimental values

System	a (Å)			B (kbar)			E_c (eV)		
	No d ^{a)}	With d ^{b)}	Exp.	No d ^{a)}	With d ^{b)}	Exp.	No d ^{a)}	With d ^{b)}	Exp.
ZnTe	5.618	6.052	6.089 ^{c)}	273	521	509 ^{d)}	6.75	5.64	4.82 ^{e)}
CdTe	5.818	6.470	6.481 ^{f)}	133	440	445 ^{g)}	6.77	5.35	4.45 ^{e)}
HgTe	5.616	6.492	6.461 ^{h)}	47	461	476 ^{g)}	7.05	4.46	3.22 ^{e)}

^{a)} Ref. [6]. ^{b)} Present study. ^{c)} Ref. [18]. ^{d)} Ref. [19]. ^{e)} Ref. [20]. ^{f)} Ref. [21]. ^{g)} Ref. [1], p. 126. ^{h)} Ref. [22].

of the d bands. Spuriously small lattice parameters and bulk moduli and probably the large cohesive energies obtained in the “no d” calculations [6] reflect the omission of the destabilizing p-d repulsions [15] (fig. 1).

(ii) In fig. 2 we show the difference between the electronic charge densities in bulk HgTe and CdTe along the bond direction. The densities are calculated self-consistently, including the cation d bands in all cases. In fig. 2a we show the density difference, omitting the contribution of the cation d bands to the density, whereas in fig. 2b the d bands are included in the density. We see that if d

states are not counted (fig. 2a) CdTe appears to have more electron density on its bond (i.e., to be more “covalent”) than HgTe. This is caused partially by the fact that the Hg 5d orbitals are considerably shallower than the Cd 4d orbitals, so that the former couple better to the anion p state, forming a stronger anti-bonding combination. This strong anti-bonding character in the valence band ($\Gamma_{15}(pd)$ in fig. 1b) of HgTe depletes the charge on the bond center, making HgTe appear spuriously ionic relative to CdTe (fig. 2a). In addition, relativistic effects [15,23] (stronger in Hg than in Cd) reduce the bonding charge on the Hg-Te bond

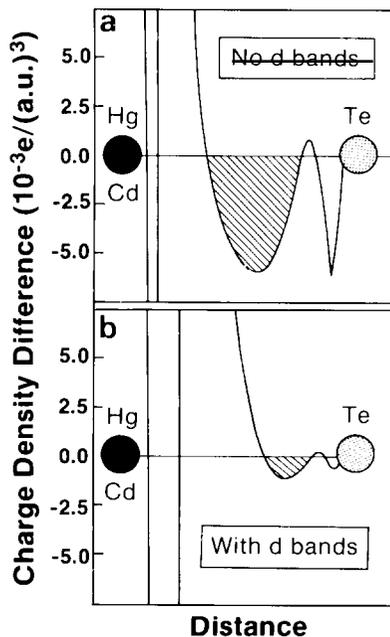


Fig. 2. Valence charge density difference between HgTe and CdTe along the cation-anion bond direction: (a) cation d bands are removed; (b) cation d bands included.

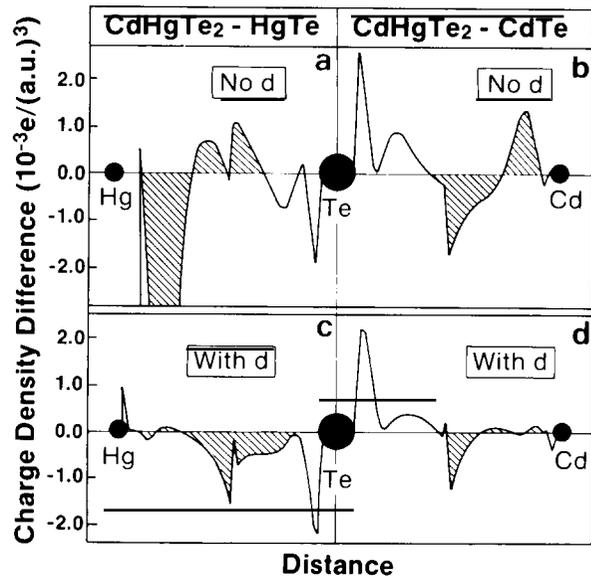


Fig. 3. Valence charge density difference between CdHgTe₂ and its binary constituents CdTe and HgTe along the cation-anion bond directions: (a) and (c) Hg-Te bond; (b) and (d) Cd-Te bond. In (a) and (b) cation d bands are removed; in (c) and (d) cation d bands are included.

relative to the Cd–Te bond. After including the cation d bands (fig. 2b), the difference becomes dramatically smaller. This is caused by the fact that the deep cation d band (the lower, $\Gamma_{15}(\text{dp})$ state in fig. 1b) in HgTe is more extended than the corresponding band in CdTe (since Hg 5d is more delocalized and less bound than Cd 4d). Adding the contribution of the deep cation d band to the charge density (fig. 2b) effectively replenishes bond charge in HgTe relative to CdTe. We conclude that omitting the d bands renders HgTe spuriously ionic relative to CdTe, but inclusion of the d bands makes both materials similarly covalent.

(iii) In fig. 3 we plot along the anion–cation bond direction the difference in charge density between the ternary compound CdHgTe_2 and its binary constituents CdTe and HgTe. If the contributions of the cation d bands to the charge densities are ignored (figs. 3a and 3b), one would erroneously conclude that in the ternary phase electron charge has *accumulated* on the Hg–Te bond (positive dashed areas in fig. 3a) and was *depleted* on the Cd–Te bond (negative dashed areas in fig. 3b). This alleged “weakening” [4] of the Hg–Te bond (relative to the Cd–Te bond) in the ternary system is but an artifact of the omission of the contributions of the cation d bands to the charge densities, as evidenced by figs. 3c and 3d, exhibiting *depletion* of bond charge on the Hg–Te bond (fig. 3c) and the Cd–Te bond (fig. 3d) in forming the ternary phase from its binary constituents. The build-up of charge on the Hg–Te bond in the absence of contributions from the deep d band (fig. 3a) is merely a consequence of a smaller p–d repulsion in CdHgTe_2 relative to HgTe. The reduced bond charge on the Hg–Te bond in the real system (fig. 3c) is due to reduced d orbital bonding in the ternary phase. Using the tight-binding method (which neglects cation d bands) Chen et al. [4] have suggested that the reduced Hg–Te bond strength in the ternary is due to an unfavorable charge transfer from Cd–Te bond (in bonding state) to Hg–Te bond (in anti-bonding state), i.e., in the opposite direction to what our calculations show. Their argument is hence not supported by our results, since we find that the charge on the Hg–Te bond is actually *reduced*.

(iv) Sher et al. [24,25] predicted that CdHgTe_2 is thermodynamically stable at low temperature, i.e., that the calculated formation enthalpy of the ordered phase

$$\Delta H = E(\text{CdHgTe}_2) - E(\text{CdTe}) - E(\text{HgTe}) \quad (1)$$

is negative (where the total energy E for the ternary and binary compounds are all calculated at their equilibrium structures). They also predicted an anomalous variation of the Cd–Te and Hg–Te bond lengths in $\text{Cd}_{1-x}\text{Hg}_x\text{Te}$ [25,26], i.e., the bond length difference between CdTe and HgTe was *increased* in the alloy, a phenomenon not observed in other semiconductor alloy systems [27]. Their predictions are supported by pseudo-potential calculation of Hass and Vanderbilt [6]. However, all of these calculations [6,24–26] neglect cation d bands. We have re-examined their results by modeling the 50%–50% alloys in the ordered “CuAu-I” structure. We have calculated the ground state properties of ZnCdTe_2 , ZnHgTe_2 and CdHgTe_2 by minimizing the total energy with respect to both the cubic lattice constant a and the anion displacement parameter [13] u which controls the relative sizes of the A–C and B–C bonds. The tetragonal distortion is assumed to be negligible (i.e., $\eta = c/a = 1$). The bond lengths

$$R_{\text{AC}} = \left(\frac{1}{8} + u_{\text{eq}}^2\right)^{1/2} a_{\text{eq}},$$

$$R_{\text{BC}} = \left[\frac{1}{8} + (0.5 - u_{\text{eq}})^2\right]^{1/2} a_{\text{eq}}$$

can then be obtained. The bulk modulus is obtained approximately by calculating the total energy as a function of volume with fixed $u = u_{\text{eq}}$. We find that, in contrast to the calculations which ignore p–d repulsion, the formation enthalpy of CdHgTe_2 is *positive* (12.3 meV per 4 atoms), indicating that the system will spinodally decompose at low temperatures (around [15] < 100 K), and that the calculated Cd–Te and Hg–Te bond lengths are essentially unchanged relative to the binaries (tables 1 and 2). We believe the discrepancies between predictions of the different calculations can be best resolved by experimental EXAFS measurements [27,28] since the 2% bond length difference predicted in the “no d” calculation [6] should be easily measurable. Our results

Table 2

Calculated ground state properties of ZnCdTe_2 , ZnHgTe_2 and CdHgTe_2 in the CuAu-I structure; the bond lengths in the binary compounds are $\frac{1}{4}\sqrt{3}a$, where a is the cubic lattice constant (table 1); i.e., $R^0(\text{Zn-Te}) = 2.621 \text{ \AA}$, $R^0(\text{Cd-Te}) = 2.802 \text{ \AA}$ and $R^0(\text{Hg-Te}) = 2.811 \text{ \AA}$

	a_{eq} (\AA)	u_{eq}	$R(\text{Zn-Te})$ (\AA)	$R(\text{Cd-Te})$ (\AA)	$R(\text{Hg-Te})$ (\AA)	B (kbar)	ΔH (meV per 4 atoms)
ZnCdTe_2	6.263	0.2290	2.638	2.790	–	440	54.3
ZnHgTe_2	6.269	0.2279	2.637	–	2.797	452	42.4
CdHgTe_2	6.481	0.2485	–	2.801	2.812	442	12.3

for ZnCdTe_2 are in good agreement with experimental data [28], where the longer bond (Cd-Te) becomes shorter and the short bond (Zn-Te) becomes longer in the ternary compounds. The more positive formation enthalpy for ZnCdTe_2 and ZnHgTe_2 (table 2) are related to the larger lattice mismatch in these systems.

(v) Because of the mixing of d character at the Γ_{15v} valence band maximum the spin-orbit (SO) splitting Δ_0 of the Γ_{15v} states is reduced relative to the “no d” limit, since d orbitals have a negative SO splitting relative to the p states. In table 3 we give the calculated Δ_0 and the angular momentum decomposed wavefunction amplitude of the Γ_{15v} states about anion and cation sites for ZnTe, CdTe and HgTe. The calculated spin orbit splittings Δ_0 for ZnTe and CdTe (0.89 and 0.86 eV, respectively) are in satisfactory agreement with the measured experimental data of 0.91 [29] and 0.90 eV [30], respectively, but the calculated Δ_0 value for HgTe (0.78 eV) is much smaller than the currently accepted value (~ 1.08 eV) [31]. Correction our Δ_0 for the fact that our cation d band is too shallow produces $\Delta_0(\text{CdTe}) = 0.91$ eV and $\Delta_0(\text{HgTe}) = 0.90$ eV, i.e. $\Delta_0(\text{HgTe})$ is still smaller than the currently accepted experimental value

[31]. A recent LMTO calculation [32] found a similar reduction, i.e., $\Delta_0(\text{HgTe}) < \Delta_0(\text{CdTe})$ (0.95 and 0.90 eV for CdTe and HgTe, respectively). The result that Δ_0 for HgTe is smaller than that for CdTe is surprising, since Hg is heavier than Cd and HgTe has a lattice constant similar to CdTe. However, it is consistent with the large d character of the HgTe Γ_{15v} state ($\sim 13\%$, see table 3). We find that without pd hybridization the calculated Δ_0 values are 0.92, 0.90 and 0.99 eV for ZnTe, CdTe and HgTe, respectively. We notice that there is no direct measurement of Δ_0 for HgTe [1] (or, equivalently, a measurement of $E_0 + \Delta_0$ and E_0 simultaneously), possibly due to the difficulty caused by the inverted band structure of HgTe [15]. A new experiment which directly measures Δ_0 is called for to resolve this question.

(vi) From fig. 1b we see that the p-d repulsion pushes the Γ_{15v} valence band maximum upward, reducing the band gap relative to the “no d” limit. This effect is largest for HgTe, for which we estimate that p-d repulsion reduces the band gap ($\Gamma_{1c} - \Gamma_{15v}$) by about 0.7 eV. Hence, calculations which omit p-d repulsion (all other things being equal) would find a larger band gap, in spuriously better agreement with experiment relative to more

Table 3

Calculated spin-orbit splitting Δ_0 at the VBM and the angular momentum decomposed wavefunction amplitude (in percentage) of the Γ_{15v} state about anion and cation muffin-tin spheres for ZnTe, CdTe and HgTe; the muffin-tin (MT) radii used are $R_{\text{MT}}(\text{Zn}) = 2.3532$ a.u., $R_{\text{MT}}(\text{Cd}) = R_{\text{MT}}(\text{Hg}) = 2.6742$ a.u. and $R_{\text{MT}}(\text{Te}) = 2.5137$ a.u.; the first row is for the anion and the second row is for the cation

	ZnTe				CdTe				HgTe			
	Δ_0	s	p	d	Δ_0	s	p	d	Δ_0	s	p	d
Γ_{15v}	0.89	0	57.3	0.2	0.86	0	55.8	0.1	0.78	0	53.8	0
		0	4.3	7.2		0	4.0	7.4		0	4.0	12.9

Table 4

Calculated and observed valence band offsets (in eV), of II–VI semiconductor pairs; the compound to the right of each pair has the higher VBM; comparison is given with the tight-binding (TB) [37] and Tersoff [38] results

	CdTe/ZnTe	CdTe/HgTe	ZnTe/HgTe	MnTe/CdTe
ΔE_{VBM} (with d) ^{a)}	0.13 ± 0.02	0.37 ± 0.03	0.26 ± 0.04	0.25 ± 0.10
Expt	0.10 ± 0.06 ^{b)}	0.35 ± 0.06 ^{c)} 0.36 ± 0.05 ^{b)}	0.25 ± 0.05 ^{b)}	
$\Delta E_{\text{VBM}}^{\text{b}}$ (TB, no d) ^{d)}	–0.07	0.00	0.07	0.04
Tersoff ^{e)}	0.01	0.51	0.50	0.75

^{a)} Present study. ^{b)} Ref. [36]. ^{c)} Ref. [35]. ^{d)} Ref. [37]. ^{e)} Ref. [38].

complete calculations which include d bands.

(vii) We have demonstrated [12] that the failure of the simple tight binding model [3] and the old “common anion rule” [33] (which suggests that the valence band offset for common anion semiconductor heterojunctions is small) in predicting valence band offsets is mainly due to the omission of pd repulsion. The basic reason for this can be appreciated from the simple model of fig. 1. Consider two semiconductors having a common anion, the same (zincblende) crystal structure, and nearly equal lattice parameters, e.g., CdTe–HgTe. If the valence band maximum were made solely from anion (p) orbitals, there would appear no reason for a substantial band offset between two such materials, since dipole-forming charge transfer is small [12]. *Cation p orbitals* can be admixed into the VBM, but this effect does not substantially discriminate one such semiconductor from the other, since the cation p orbital energies are similar in the Hg–Cd pair [3]. *Cation d orbitals* can, however, induce a band offset: since the amount by which the VBM of a given material is pushed upwards by p–d repulsion is inversely proportional to the anion–cation energy difference $\epsilon_{\text{a}}^{\text{p}} - \epsilon_{\text{c}}^{\text{d}}$, materials with shallow d states (HgTe) have their VBM higher in energy than materials with deeper d energies (CdTe). We have calculated [12] the valence band offsets of the four common-anion semiconductors CdTe/HgTe, CdTe/ZnTe, ZnTe/HgTe and MnTe/CdTe [13,34] in a way that parallels their measurement in photoemission core-level spectroscopy [35]. Three quantities are needed in such a calculation. The core level binding energies $E_{n'l,A}^{\text{AC}}$ and $E_{n'l',B}^{\text{BC}}$ of the cations A and B, respectively relative to the VBM, (obtained

from the band structures of AC and BC, respectively) and the core level difference $\Delta E_{n'l,n'l'}^{\text{A,B}}$ (calculated from the band structure of the (001) (AC)₁(BC)₁ superlattice, which is equivalent to the ABC₂ “CuAu-I” structure). We have shown [12], using a simple electrostatic model, that for common anion systems interface dipole effects are small and localized near the interface, so that an ultrathin superlattice is sufficient to obtain the core level difference $\Delta E_{n'l,n'l'}^{\text{A,B}}$. The valence band offset ΔE_{VBM} is then obtained as:

$$\Delta E_{\text{VBM}} \cong E_{n'l,A}^{\text{AC}} - E_{n'l',B}^{\text{BC}} + \Delta E_{n'l,n'l'}^{\text{A,B}}. \quad (2)$$

We find that [12] after including p–d hybridization our calculated valence band offsets are in good agreement with experimental data [35,36]. Our results (with d) are compared with tight binding (TB) calculation [37] (no p–d repulsion) and experimental data for CdTe/ZnTe, CdTe/HgTe, ZnTe/HgTe and MnTe/CdTe in table 4. We also listed results obtained by Tersoff [38], whose theory emphasizes the importance of the interface dipole contribution to the valence band offset. Our results and analysis indicates that the assertion that interface dipole effects are needed to obtain the correct valence band offset is not tenable.

5. Conclusion

We have demonstrated through first principles total energy and electronic structure calculations of II–VI compounds and their alloys that p–d hybridization in II–VI systems is crucial for understanding the structural and electronic properties of these systems.

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