



: jfghdfjbWjd`Yg`WJ`W`Uhjcb`cZVUbX`cZgYhgžcdh]WJ`Vck]b[gžUbX`XYZYWg]b`7XGž7XGYž
7XHYžUbX`h\Y]f`U`cmg

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I. INTRODUCTION

Cd-based II-VI semiconductor compounds and alloys have attracted considerable interest in the last few years due to their applications in photovoltaic devices.^{1,2} CdTe has an ideal band gap and high absorption coefficient which makes

=5.818, 6.052, and 6.482 Å for CdS, CdSe, and CdTe, respectively, for electronic structure calculations. The LDA calculated lattice constants¹⁸ are within 0.7% of the experimental values.

A. Band offsets

To calculate the valence band offset $DE_v(\text{CdX}/\text{CdY})$ at the interface between two Cd compounds CdX and CdY we follow the procedure^{7,8} used in photoemission core-level spectroscopy, where the band offset is given by

$$DE_v(\text{CdX}/\text{CdY}) = DE_{\text{VBM},\text{C}}^{\text{CdX}} - DE_{\text{VBM}',\text{C}'}^{\text{CdY}} + DE_{\text{C},\text{C}'}$$

Here, $DE_{\text{VBM},\text{C}}^{\text{CdX}} = E_{\text{VBM}}^{\text{CdX}} - E_{\text{C}}^{\text{CdX}}$ is the core level to valence band maximum energy separations for CdX and $DE_{\text{C},\text{C}'} = E_{\text{C}}^{\text{CdX}} - E_{\text{C}'}^{\text{CdY}}$ is the difference in core level binding energy between CdX and CdY on each side of the interface. To obtain the unstrained band offset, the first two terms in Eq. 1 are calculated at their respective equilibrium structural parameters appropriate to the isolated compounds. The core level difference $DE_{\text{C},\text{C}'}$ between the two Cd compounds is obtained from the calculation for the $(\text{CdX})_n/(\text{CdY})_n$ superlattices with (001) orientation. The superlattice layer thickness n is increased until the core levels of the innermost layer on each side of the superlattice are bulk-like. The small orientational dependence and strain dependence of the core levels¹⁹ are neglected. The uncertainty in the calculated valence band offset is about 0.05 eV. A compilation of predicted valence band offsets of all II-VI and III-V systems is given in Ref. 8.

The method of Eq. 1 necessitates not only calculation of bulk CdX and CdY, but also the CdX/CdY heterojunction. In this sense, it is more accurate than the ‘‘model solid’’ method of Van de Walle²⁰ or the ‘‘dielectric midgap level’’ approach of Cardona and Christensen²¹ in that these methods all *assume*

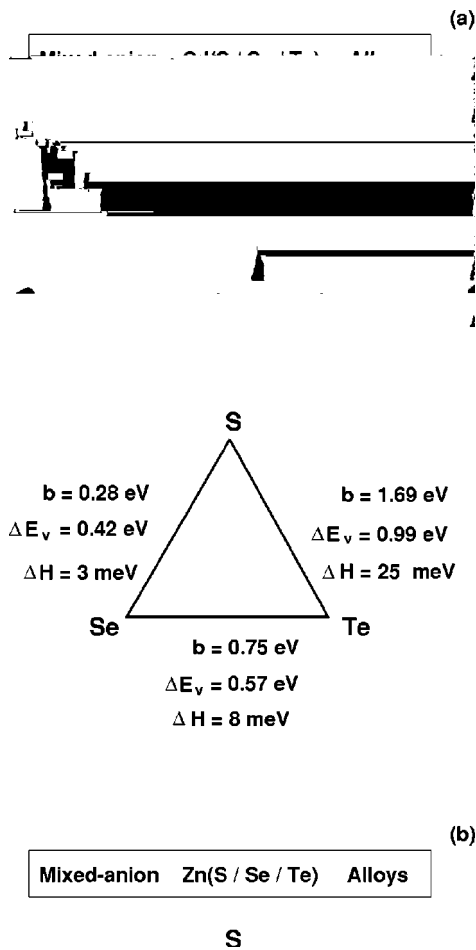


FIG. 1. Calculated bowing coefficients b , valence band offsets ΔE_v , and alloy mixing energies ΔH at $x=1/2$ of Cd-based alloys. ΔH is given in meV per atom. Results for Zn-based alloys are also included for comparison.

The “defect transition energy level” $e_a(q/q')$ is the Fermi energy e_F in Eq. (3) at which the formation energy $DH_f(a, q)$ of defect a of charge q is equal to that of another charge q' of the same defect, i.e.,

$$e_{a-q/q'} = DE_{a,q} - DE_{a,q'} \quad (5)$$

For example, $e_a(-/0)$ is an acceptor level. When e_F is below $e_a(-/0)$ the defect a is neutral, while defect a is negatively charged when e_F is above $e_a(-/0)$. $e_a(q/q')$ tells us where in the gap can we find the donor and acceptor levels of defect a .

Due to the small cell-size and small basis set used in the present calculation we estimate that the error in the calculated formation energies is about 0.2 eV and the error in the calculated transition energies is about 0.1 eV. LDA error in the band gap error further introduce uncertainties in the calculated results, especially for the deep levels.

III. RESULTS

Figure 1 summarizes ΔH , b , and ΔE_v for CdS, CdSe, and CdTe. For comparison, we repeat the corresponding values³¹ for ZnS, ZnSe, and ZnTe in Fig. 1b. We next discuss the salient features in Fig. 1.

A. Mixing enthalpies

The mixing enthalpy of the random $\text{CdX}_x\text{Y}_{1-x}$ alloy at $x=0.5$ can be obtained from the calculated alloy total energies as

$$DH_{x=1/2} = E_{\text{tot}}(\text{CdX}_{0.5}\text{Y}_{0.5}) - \frac{1}{2}E_{\text{tot}}(\text{CdX}) - \frac{1}{2}E_{\text{tot}}(\text{CdY}) \quad (6)$$

Our calculated values (in meV/atom) are denoted as ΔH in Fig. 1-a. We find the following results:

i) The mixing enthalpies are all positive and increases as the lattice mismatch between the constituents increases. For example, $\Delta H(\text{CdS}_{0.5}\text{Se}_{0.5})$, $\Delta H(\text{CdSe}_{0.5}\text{Te}_{0.5})$, and $\Delta H(\text{CdS}_{0.5}\text{Te}_{0.5})$ are 3, 8, and 25 meV/atom, respectively, and the corresponding size-mismatches $\Delta a/\bar{a}$ are 3.8%, 6.9%, and 10.7%, respectively. For Zn alloys, the corresponding lattice mismatch are 4.6%, 7.2%, and 11.8%, respectively. The positive sign of ΔH indicates that the ground state of these alloys at $T=0$ corresponds to phase separation into the binary zinc-blende constituents. However, at finite temperatures, the disordered phase can be stabilized through entropy. The mixing enthalpy ΔH is rather small for $\text{CdS}_x\text{Se}_{1-x}$ alloy, suggesting that $\text{CdS}_x\text{Se}_{1-x}$ will be miscible in the whole composition range at finite temperatures. The mixing enthalpy ΔH is large for the $\text{CdS}_x\text{Te}_{1-x}$ alloy, suggesting that large miscibility gap exist in $\text{CdS}_x\text{Te}_{1-x}$ e.g., using the regular solution model, where the free energy F is given by $F = Vx(1-x) + kT[x \ln x + (1-x) \ln(1-x)]$ and $V = 4\Delta H(x=0.5)$, we estimate that the miscibility is about 8% at $T=800$ K.

ii) Cd alloys have smaller mixing enthalpies than the corresponding Zn alloys. This is mainly due to the smaller lattice mismatch and smaller bulk moduli¹⁸ of the Cd alloys -thus, smaller elastic strain energies relative to the Zn alloys.

B. Band offsets

Using the procedure described in Sec. II A we have calculated the unstrained natural valence band offsets between the cubic II-VI CdS/CdSe/CdTe compounds (Fig. 2). The conduction band offsets ΔE_c are obtained using the relation

$$\Delta E_c = \Delta E_g + \Delta E_v \quad (7)$$

where ΔE_g is the measured^{17,30} band gap differences between the compounds. We find the following results:

i) The S/Se unstrained band lineup is “type I,” while the S/Te and Se/Te band lineup is “type II.”

ii) The band offsets are large in the valence band, but small in the conduction band. The large valence band offsets for this mixed anion system are consistent with the fact that the VBM is anion p -like state, and that the anion p orbital energies increase significantly as anion atomic number increases (Table II). The small conduction band offsets are also consistent with the fact that CBM is mostly cation s states with only minor contributions from anion s orbitals. It is interesting to see that the order of the CBM in CdX follow the same trend as the anion X s atomic orbital energies (Table II).

-iii! The valence band offsets between the Cd compounds are smaller than those between the corresponding Zn compounds -Fig. 1!. The reason⁷ is as follows: In the zincblende compound with T_d site symmetry both the anion p and the cation d orbitals transform -among others! as the G_{15} -also called t_2) representation. These two equal-symmetry states interact with each other, in direct proportion to the $p-d$ coupling matrix element and in inverse proportion to the energy difference $e_p^{\text{anion}} - e_d^{\text{cation}}$. The interaction between the anion p and the occupied cation d states results in a level repulsion, moving the VBM *upwards*.⁷ This $p-d$ coupling tends to *reduce* the valence band offsets.⁸ This is so since the S p orbital is deeper -i.e., closer to the metal d orbital! than the Se p

size mismatch and chemical disparity in VBM in Cd compounds lead to a smaller bowing in Cd alloys than in the Zn alloys.

-iii! For most semiconductor alloys the bowing coefficient b is nearly independent of composition x .^{17,43} However,

b

The calculated $\sim +/0!$ transition energy levels is at $E_v + 0.18$ eV for isolated CdS:Te impurity. The donor level $\sim +/0!$ is at $E_v + 0.42$ eV for Te-Te nearest neighbor impurity pairs. These results can be compared with experimental data of 0.22 and 0.44 eV, respectively, derived from photoluminescence measurements.⁵¹⁻⁵⁴ We see that the general agreement is good. The smaller calculated values relative to the measured values could be caused by the LDA error in the band gap.

E. Defect formation energies and defect transition energy levels

CdTe is the only II-VI compound which can be doped relatively easily either p or n type.⁵⁵ Many of the devices, e.g., solar cells use p -type CdTe as absorber.^{1,2} Beside defect pairs such as the A center,⁵⁶ the leading candidates of the p -type dopant in CdTe is Cd vacancy V_{Cd} and Cu substitution on Cd sites Cu_{Cd} . Using the method described in Sec.

leading to a diffusion of Cu atom from the *p*-CdTe layer to the *n*-CdS layer. This type of Cu diffusion has been observed experimentally in CdS/CdTe solar cells.⁵⁷

-ii! V_{Cd} formation energy: For neutral V_{Cd}^0 defect the calculated defect formation energy at $m_{Cd}=0$ is 4.10 eV for CdS and 2.30 eV for CdTe. For the singly negatively charged defect V_{Cd}^- , DH is 4.43 eV for CdS and 2.42 eV for CdTe; and for the doubly negatively charged defect V_{Cd}^{2-} , it is 4.94 eV for CdS and 2.69 eV for CdTe, if the Fermi energy is taken at their respective VBM -Fig. 5!. Again, we find that if we use a common Fermi energy in an absolute energy scale, and let $E_F = E_{VBM}(CdS) + 0.99$ eV $= E_{VBM}(CdTe)$, the formation energy of the closed shell defect V_{Cd}^{2-} in CdS is 2.96 eV, similar to the 2.69 eV found in CdTe. The fact that, using an absolute energy scale for the Fermi energy, the formation energies of certain closed shell defects -e.g., Cu_{Cd}^- and V_{Cd}^{2-}) are similar in a class of material -e.g., CdX! @thus, similar $e_{pin}^{(n)}$ # has also been found in another system.¹⁰ This phenomena has been described in Ref. 10 and is used to explain the phenomenological “doping limit rule” in semiconductors and insulators.

-iii! Since the formation energies of Cu_{Cd} is smaller than V_{Cd} , presence of Cu in the sample is expected to eliminate the V_{Cd} defect. To aid the search of the Cu_{Cd} substitutional defect we have calculated the Cu-X bond length in CdX compounds. We find that the Cu-X bond lengths are about 6.7% smaller than the Cd-X bond lengths.

-iv! Cu_{Cd} transition energy levels: The calculated Cu_{Cd} -0/-! transition energy levels is $E_{VBM} + 0.64$ eV for CdS and $E_{VBM} + 0.14$ eV for CdTe!

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