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Electronic Structure Theory of Chalcopyrite Alloys, Interfaces, and Ordered Vacancy Compounds

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Abstract. This paper summarizes recent results of an ongoing project in which first principles band structure theory is used to systematically predict the basic materials properties of photovoltaic chalcopyrite semiconductors. Here we discuss the (i) chalcopyrite alloy band gap bowing coefficients, (ii) chalcopyrite alloy mixing enthalpies, (iii) interfacial valence and conduction band offsets between mixed-anion (CuInX_2 , $X = \text{S, Se, Te}$) and between mixed-cation (CuMSe_2 , $M = \text{Al, Ga, In}$) chalcopyrite interfaces, and (iv) electronic structures of the “ordered vacancy compounds”. Results are provided as predictions to be tested experimentally. We find that the strong Cu d - anion p coupling controls much of the electronic properties of the chalcopyrite alloys and distinguishes them from Zn or Cd based II-VI's.

I. Introduction

Solar cells based on chalcopyrite materials have developed rapidly from 5% efficiency in 1974 to about 16% at present. The recent progress of high efficiency solar cells is achieved by alloying [1-3] CuInSe_2 (CIS) with either CuGaSe_2 or with CuInS_2 . The structural, transport, and optical properties of the alloys can be tuned continuously by varying the relative composition. The observed [2,3] homojunction between CuInSe_2 and Cu-poor ordered vacancy compounds (OVC) appears to play important role in the photovoltaic process. While the properties of some of the end-point chalcopyrites are known, little is known about (a) the properties of alloys between any two members of $\text{CuInS}_2/\text{CuInSe}_2/\text{CuInTe}_2$ or $\text{CuAlSe}_2/\text{CuGaSe}_2/\text{CuInSe}_2$ and (b) of the OVC. We have calculated [4] the (i) alloy bowing coefficient, (ii) alloy mixing enthalpy, (iii) valence and conduction band lineups at the relaxed interface between mixed cation $\text{CuAlSe}_2/\text{CuGaSe}_2/\text{CuInSe}_2$ and mixed anion $\text{CuInS}_2/\text{CuInSe}_2/\text{CuInTe}_2$ chalcopyrites, and (iv) electronic structures of the OVC. This paper briefly describes how such calculations are done and discusses the significant physics of the results. More details are given in Refs. [4-8].

II. Method of Calculation

(a) *Total energies:* Total energy and band structure calculations were performed using the density functional formalism [9,10] as implemented by the general potential, relativistic, all electron, linearized augmented plan wave (LAPW) method [11]. The lattice constant and the unit cell internal structural parameters are obtained in the calculation through the minimization of total energy and quantum mechanical

force on all atoms.

(b) *Alloy bowing*: Random A_xB_{1-x} alloys of different chalcopyrites are modeled using the efficient special quasirandom structures (SQS) approach [12]. In this approach, rather than occupy sites of a huge unit cell by mixed A and B atoms *at random*, one occupies the sites of a “small” unit cell so that the first few atom-atom correlation functions are forced to be close to the exact values in an infinite random alloy. For both *mixed-anion chalcopyrite alloys* [e.g., $\text{CuIn}(\text{S}_{0.5}\text{Se}_{0.5})_2$], and Cu based *mixed-cation chalcopyrite alloys* (e.g. $\text{CuGa}_{0.5}\text{In}_{0.5}\text{Se}_2$), we use a 16-atom SQS unit cell.

(c) *Band offsets*: The valence band offset $\Delta E_v(ABX_2/A'B'X'_2)$ at the interface between two chalcopyrites ABX_2 and $A'B'X'_2$ is calculated using an analogous procedure [6,8] employed in the photoemission core-level spectroscopy: The band offset is given by $\Delta E_v = \Delta E_{\text{VBM},\text{C}}^{ABX_2} - \Delta E_{\text{VBM}',\text{C}'}^{A'B'X'_2} + \Delta E_{\text{C},\text{C}'}$. The first two terms on the right hand side are the core-level to valence band maximum energy separations for ABX_2 and $A'B'X'_2$, respectively, and the last term is the difference in core level binding energy between ABX_2 and $A'B'X'_2$ on each side of the interface. The core-to-VBM energy difference $\Delta E_{\text{VBM},\text{C}}$ is obtained as a difference in band energies between the component chalcopyrites calculated at their respective equilibrium structural parameters appropriate to the isolated compounds. The core energy level difference $\Delta E_{\text{C},\text{C}'}$ between the two chalcopyrites is obtained from the calculation for the $(ABX_2)_n/(A'B'X'_2)_n$ superlattice with (001) orientation. The conduction band offsets ΔE_c are obtained using the relation $\Delta E_c = \Delta E_g - \Delta E_v$, where ΔE_g is the *measured* band gap difference between the compounds (so local density error do not affect the results).

(d) *Ordered Vacancy Compounds*: Various CuInSe_2 -derived defect structure can exist in a CuInSe_2 -based solar cell [2,3]. In this paper, we limit our study to the substitutional Cu -poor CuInSe_2 -based OVC. In selecting candidate OVC crystal structures, we employed the following conditions: (i) The high energy anion-cation antisite defects (Cu_{Se} , In_{Se} , Se_{Cu} , and Se_{In}) are not allowed. (ii) Defects and atomic rearrangement were allowed to occur only on the Cu sublattice, so V_{Se} , V_{In} , and Cu_{In} are not allowed. (iii) The OVC are assumed to be charge compensated, i.e., the tie-line condition $K + 3L = M/2$ is assumed to be satisfied, where K , L , and M are number of Cu_{Cu} , In_{Cu} , and Se_{Se} atoms, respectively. This charge compensation

TABLE I. Examples of the charge compensated ordered vacancy compounds, see text for details.

Cu_{Cu}	In_{Cu}	In_{In}	Se_{Se}	V_{Cu}	Formula	Symbol	x
K	L	K+3L	2(K+3L)	2L			
1	0	1	2	0	CuInSe_2	CIS	1.0
1	1	4	8	2	$\text{Cu}_1\text{In}_5\text{Se}_8[\text{V}_{\text{Cu}}]_2$	OVC-1:5:8	0.0
2	1	5	10	2	$\text{Cu}_2\text{In}_6\text{Se}_{10}[\text{V}_{\text{Cu}}]_2$	OVC-1:3:5	0.2
3	1	6	12	2	$\text{Cu}_3\text{In}_7\text{Se}_{12}[\text{V}_{\text{Cu}}]_2$	OVC-3:7:12	1/3
4	1	7	14	2	$\text{Cu}_4\text{In}_8\text{Se}_{14}[\text{V}_{\text{Cu}}]_2$	OVC-2:4:7	3/7
6	1	9	18	2	$\text{Cu}_6\text{In}_{10}\text{Se}_{18}[\text{V}_{\text{Cu}}]_2$	OVC-3:5:9	5/9

requirement also indicates that in the OVC each In_{Cu} antisite must be accompanied by two V_{Cu} (Cu vacancies). Examples of the OVC which satisfy conditions (i)-(iii) are given in Table I. Each entry in Table I can exist in many different atomic configurations. We select those that minimize the total energy. To keep the deviation from the octet rule to a minimum, we retain only three types of local tetrahedral clusters around each Se: $2\text{Cu}+2\text{In}$ (called $n=8$), $\text{V}_{\text{Cu}}+\text{Cu}+2\text{In}$ (called $n=7$), and $\text{V}_{\text{Cu}}+3\text{In}$ (called $n=9$). The latter two occur in equal proportions so as to maintain charge compensation. An OVC is an weighted distribution of these three clusters. For examples, CuInSe_2 in the chalcopyrite structure consists of 100% of the $n=8$ clusters; CuIn_5Se_8 (OVC-1:5:8) consists of 50% of the $n=7$ and 50% of the $n=9$ clusters. CuIn_3Se_5 (1:3:5) has 20% of the $n=8$ cluster and 40% each of the $n=7$ and $n=9$ clusters. As one can see, this class of OVC can also be described as a fictitious alloy of $(\text{Cu}_4\text{In}_4\text{Se}_8)_x(\text{CuIn}_5\text{Se}_8)_{1-x}$. Table I gives the x values

III. Results

(a) *Mixing enthalpies of chalcopyrite alloys:* The mixing enthalpy of random chalcopyrite alloys can be obtained from the calculated alloy total energies E_{tot} as $\Delta H = E_{tot}(\text{ABX}_2/\text{A}'\text{B}'\text{X}'_2) - E_{tot}(\text{ABX}_2) - E_{tot}(\text{A}'\text{B}'\text{X}'_2)$. Our calculated results are denoted as ΔH in Fig. 1. We find that for both mixed-anion and mixed-cation alloys the mixing enthalpy is positive and increases as the lattice mismatch increases. For example, $\Delta H(\text{S,Se})$, $\Delta H(\text{Se,Te})$, and $\Delta H(\text{S,Te})$ equal 3, 13, and 41 meV/atom, respectively, corresponding to the size-mismatches $\Delta a/\bar{a}$ 4.6%, 6.3%, and 10.9%, respectively. The positive sign of ΔH indicates that the alloy ground state at $T = 0$ corresponds to phase separation into the pure chalcopyrite constituents. (However, at finite temperatures, the disordered phase can be stabilized by entropy.) The mixing enthalpy ΔH is rather small for (S,Se) and (Al,Ga) chalcopyrite alloys, and is slightly larger for (Se,Te), (Ga,In), and (Al,In) alloys. The rather small values of ΔH for the (S,Se), (Al,Ga), (Se,Te), and (Ga,In) alloys suggest that these chalcopyrite alloys will be miscible in the whole composition range at preparation temperatures. The mixing enthalpy ΔH is large for the (S,Te) alloy, suggesting that large equilibrium miscibility gap and atomic clustering can exist in this system.

Band offsets of chalcopyrite alloys: Figure 2a gives the *unstrained* valence band offsets between the common-cation $\text{CuInS}_2/\text{CuInSe}_2/\text{CuInTe}_2$ chalcopyrites, while Figure 2b gives results for the common-anion $\text{CuAlSe}_2/\text{CuGaSe}_2/\text{CuInSe}_2$ chalcopyrites. We find the following results: (i) The S/Se band lineup is “type I”, while the S/Te and Se/Te band lineups are “type-II”. For the mixed-cation chalcopyrites, the lineup is always type-I. (ii) For common-cation chalcopyrites (Fig. 2a) the band offsets are large both in the valence band and in the conduction band. (iii) For common-anion chalcopyrites (Fig. 2b) most of the band offset is in the conduction band. The valence band offset is small, indicating that the “common-anion rule” (which suggests that the valence band offset for the common-anion system should be small) is followed rather well for this system. (iv) We find that for both common-cation and common-anion chalcopyrite interfaces, the transitivity rule holds for the intrinsic unstrained band offsets, i.e., $\Delta E_v(A/B) = \Delta E_v(A/C) + \Delta E_v(C/B)$. Assuming that this transitivity rule also holds for an unstrained interface between a II-VI window material compound and a chalcopyrite absorber, our present results

can be combined with our earlier studies [6] of the band offsets between CuInSe_2 and II-VI (CdS and ZnSe) to predict other band offsets between a chalcopyrite compound and a II-VI compound. For example, our calculated [6,8] ΔE_v between CuInSe_2 and CdS is 1.07 eV, and ΔE_v between CuInSe_2 and CuGaSe_2 is 0.04 eV (Fig. 2b), thus we expect that ΔE_v between CuGaSe_2 and CdS should be 1.03 eV. Similarly, since $\Delta E_v(\text{CuInS}_2/\text{CuInSe}_2) = 0.28$ eV, then ΔE_v between CuInS_2 and CdS should be around 0.79 eV. In some cases (e.g., $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$) one may also assume that the VBM of the alloy is a linear function of composition x , hence one

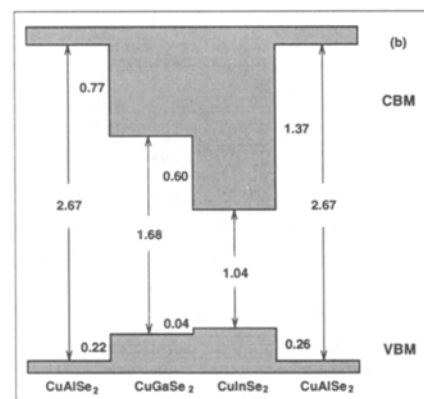
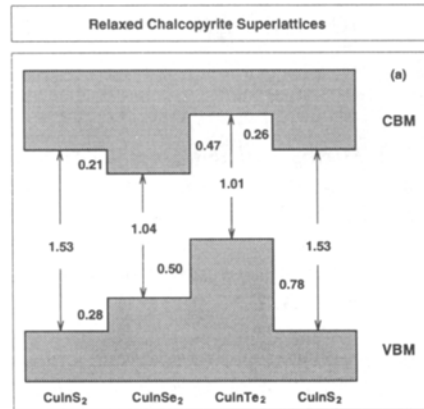
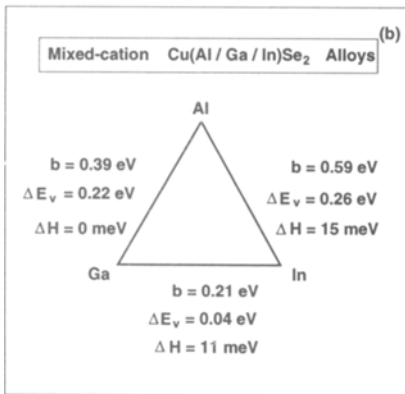
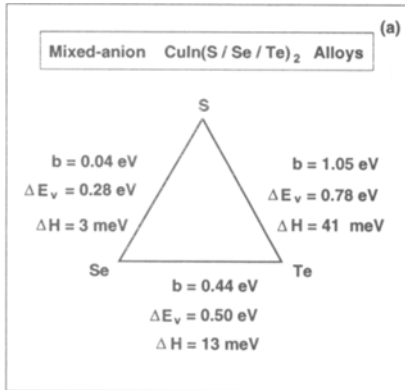


Fig. 1. Calculated bowing coefficients b , unstrained valence band offsets ΔE_v , and bulk alloy mixing energies ΔH at $x = 1/2$ (in meV/atom) of (a) mixed-anion chalcopyrite alloys and (b) mixed-cation chalcopyrite alloys.

Fig. 2. Calculated unstrained valence band and conduction band offsets for interfaces between (a) common-cation chalcopyrite compounds and (b) common-anion chalcopyrite compounds.

can roughly estimate the band offset between a chalcopyrite *alloy* and a II-VI compound.

(c) *Optical bowing of chalcopyrite alloys*: The optical bowing parameter b of the chalcopyrite alloy is given by $b = -4[E_g(ABX_2/A'B'X'_2) - 1/2E_g(ABX_2) - 1/2E_g(A'B'X'_2)]$. Figure 1 gives the calculated bowing parameter for stoichiometric mixed-anion (Fig. 1a) and mixed-cation (Fig. 1b) chalcopyrite alloys. Our calculated results agrees well with recent experimental data (see discussion in Ref. 4). Optical bowing in semiconductor alloys is caused [12] by (i) the difference in volume deformation potentials of the constituents and (ii) the coupling between the folded states by the perturbation potential ΔV , representing the difference between the alloy potential and the average potential of the constituents. When the constituents have large difference in their atomic potential or large difference in their size, ΔV is large, thus the optical bowing is expected to be large.

In the mixed-anion alloys (Fig. 1a), CuIn(S,Se) has a rather small bowing, while the bowings for CuIn(Se,Te) and CuIn(S,Te) are large. The trend $b(S, Se) < b(Se, Te) < b(S, Te)$ is observed in chalcopyrite alloys.

In the mixed-cation alloys (Fig. 1b) Cu(Al,Ga)Se₂ and Cu(Al,In)Se₂ alloys have relatively larger bowing coefficients ($b = 0.39$ and 0.59 eV, respectively) than Cu(Ga,In)Se₂ ($b = 0.21$ eV). This is mainly due to the difference of the $p-d$ coupling [4] between Al compounds (with unoccupied d orbital) and Ga or In compounds (with occupied d orbitals).

(d) *Electronic structure of the OVC*: The crystal structures of the OVC are not well understood at present. By minimizing the calculated first-principles total energy and atomic force we have first studied the crystal structures of CuInSe₂ and the OVC CuIn₅Se₈. For CuInSe₂ we find [5] the chalcopyrite structure is the ground state configuration, in agreement with experiment. The calculated lattice constant $a = 5.751$ Å agrees to within 0.6% with the experimental value [13]. For CuIn₅Se₈ we find that the minimum energy crystal structure corresponds to a stacking of Cu/V_{Cu}/In_{Cu}/V_{Cu} (110) planes in the Cu sublattice of the chalcopyrite CuInSe₂. The calculated lattice constant of CuIn₅Se₈ is 5.663 Å, close to the value for GaAs ($a=5.653$ Å). This indicates that use GaAs as a substrate can stabilize the growth of CuIn₅Se₈. We find that in the OVC the Cu-Se and In-Se bond lengths are similar to their ideal values in CuInSe₂, while the Se-V_{Cu} distance is about 10% shorter than the Cu-Se bond length.

Figure 3 show our calculated band alignment between CuInSe₂ and the OVC CuIn₅Se₈. Our previous results [6] for the CdS/CuInSe₂ interface are also included for comparison. We find that the unstrained VBM of CuInSe₂ is 0.42 eV higher than that of CuIn₅Se₈. This is due to stronger $p-d$ coupling in CuInSe₂ than in CuIn₅Se₈. The calculated band gap of CuIn₅Se₈ is 0.34 eV *larger* than for CuInSe₂, so

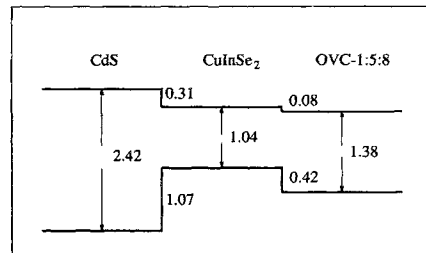


Fig. 3. Calculated valence band and conduction band offsets (in eV) between CdS, CuInSe₂ and CuIn₅Se₈ (OVC-1:5:8).

the CBM of CuIn_5Se_8 is 0.08 eV lower than for CuInSe_2 . Since many of the charge-compensated OVC can be formally written as an alloy in the form $(\text{Cu}_4\text{In}_4\text{Se}_8)_x(\text{CuIn}_5\text{Se}_8)_{1-x}$ (see Table I), the band alignment between any of these OVC and CuInSe_2 can be linearly interpolated from the values given in Fig. 3. For instance, for the OVC CuIn_3Se_5 ($x = 0.2$), we estimate that its VBM and CBM are 0.34 eV and 0.06 eV lower than CuInSe_2 , respectively. These predictions agrees very well with the recent measurement of Schock and Stolt [3], who find the corresponding values are 0.28 and 0.02 eV, respectively.

IV. Summary

Using first-principles band structure theory we have studied systematically electronic structure of chalcopyrite alloys, interfaces and ordered vacancy compounds. Experimental investigations of our predicted results are called for.

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