REVISITING THE DEFECT PHYSICS IN CuInSe$_2$ AND CuGaSe$_2$

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ABSTRACT

Using first-principles self-consistent electronic structure theory, we have calculated defect formation energies and defect energy levels in CuInSe$_2$. Contrary to previously accepted assumptions in the analysis of defects in CuInSe$_2$ we find that (i) it is much easier to form Cu vacancy in CuInSe$_2$ than to form cation vacancies in II-VI's. (ii) Defect formation energies vary considerably both with the Fermi energy and the chemical potential of the atomic species, and (iii) Defect pairs such as $(2V_{Cu} + In_{Cu})$ have a remarkably low formation enthalpy. This explains the massive non-stoichiometry of CuInSe$_2$ and the appearance of ordered defect compounds CuIn$_5$Se$_8$, CuIn$_3$Se$_5$, Cu$_2$In$_4$Se$_7$ and Cu$_3$In$_5$Se$_9$. The fact that CuInSe$_2$ has good electrical properties despite this off-stoichiometry reflects the mutual passivation of In_{Cu} by V_{Cu}. Similar results are found for CuGaSe$_2$, except that (iv) it is more difficult to form $(2V_{Cu}^- + Ga_{Cu}^{2+})$ in CuGaSe$_2$ than to from $(2V_{Cu}^- + In_{Cu}^{2+})$ in CuInSe$_2$, and (v) the Ga_{Cu} donor levels are much deeper than the In_{Cu} donor levels. Thus, it is more difficult to dope CuGaSe$_2$ n-type.

INTRODUCTION

CuInSe$_2$, a prototype member of the family of I-III-VI$_2$ chalcopyrite semiconductors [1], is the key semiconductor material for thin film solar cell applications, having achieved 17% efficiency in polycrystalline form by alloying it with CuGaSe$_2$ [2,3]. Unlike the analogous II-VI binary compounds, CuInSe$_2$ shows three unusual defect-related features:

(a) *Structural tolerance to large off-stoichiometry:* CuInSe$_2$ and other chalcopyrites appear to tolerate a large range of anion-to-cation off-stoichiometry (i.e., samples with a few percentage Cu-poor and/or In-poor stoichiometries are stable [4]. The extreme limit of "off-stoichiometry" is manifested by the existence of a series of compounds with different Cu/In/Se ratios [5]—CuIn$_5$Se$_8$, CuIn$_3$Se$_5$, Cu$_3$In$_5$Se$_9$,etc.—, absent in II-VI compounds or their solid solutions such as Zn$_{1-x}$Cd$_x$Se or ZnS$_{1-x}$Se$_x$.

(b) *The ability to dope CuInSe$_2$ via native defects:* CuInSe$_2$ can be doped p and n type to a low-resistivity level merely via introduction of *native* defects, without extrinsic impurities [6,7]. For example, p-type samples can be created by making the sample Cu-poor or via anneal in the *maximum* Se pressure, while n-type samples can be made by making the sample Cu-rich, or via anneal in *minimum* Se pressure [7]. In contrast, the (small) off-stoichiometry attainable in II-VI sulphides and selenides often leads to *deep* levels, inducing in the sample *high* electrical resistivity.

(c) *The electrically benign nature of the structural defects:* While in ordinary III-V and II-VI semiconductors, polycrystallinity leads to a high concentration of electrically-active (grain-boundary) defects that have a very detrimental effect on the performance of optoelectronic devices, polycrystalline CuInSe$_2$ is as good an electronic material as its single-crystal counterpart, even though it has many non-stoichiometry defects [8].

The three puzzles regarding the defect structure of CuInSe$_2$ are technologically beneficial. They led to the utilization of CuInSe$_2$ in low-cost (i.e., polycrystalline) devices [2,3,8], and, at the same time, to many attempts to understand these unusual phenomena [9-13]. Yet, despite extensive and successful efforts at *characterization of the defect levels* in CuInSe$_2$, very little evidence exists as to the chemical and structural *identification of the defect centers* producing those levels. Our current understanding of defects in III-Vs (e.g., DX, EL2 or transition-metal impurities) and in II-VIs (e.g., N doping of p-type ZnSe) owes its clarity to a beneficial interaction of fundamental characterization experiments with modern, first-principles theoretical calculations. Such calculations have been impossible for many years for *ternary* systems containing active d-electron elements (Cu). In the absence of reliable theory, the field has taken a different turn: the many defect levels observed experimentally to exist in CuInSe$_2$ were assigned to particular defects (e.g., V_{Cu}, V_{In}, Cu_i, Cu_{In} ...) based on "intuition" and on the perceived abundance of such defectss. The abundance of particular defects was guessed from the generalization of the cavity model of Van Vechten [14] which uses empirical atomic radii and model bond energies as input. Although these studies [9-12] provide some insights into the the understanding of defect physics in CuInSe$_2$, they neglected the dependence of the defect formation energies on the chemical potentials and Fermi levels, and considered only point-defect (no complexes). As a result, they have serious shortcomings. For example, using this model, Neumann [9] found that (i) cation vacancy formation energies in chalcopyrite is larger than in II-VIs, and (ii) In_{Cu} antisite has low formation energy than Cu vacancy V_{Cu}. As a result, it was thought that Cu vacancies are not prevalent in CuInSe$_2$ and In_{Cu} is very abundant.

Naturally, observed defect levels were assigned to In_{Cu}.

Due to a series of theoretical and computational developments, it is now possible to apply first-principles quantum mechanics to the prediction of defect properties of ternary materials with d electrons. In this study we use the first-principles self-consistent electronic structure theory to calculate the formation energies and electrical transition levels of point defects and defect pairs and arrays in CuInSe$_2$ [15]. We show that, contrary to previous assumptions common in the analysis of defects in CuInSe$_2$, (i) it is much easier to form Cu vacancy in CuInSe$_2$ than to form cation vacancies in II-VI's, (ii) defect formation energies vary considerably both with the Fermi energy and the chemical potential of the atomic species, and (iii) defect pairs are abundant in CuInSe$_2$, altering their electric activity. We explain puzzles (a)-(c) above as follows:

(a) *Structural tolerance to large off-stoichiometry:* The large concentration of off-stoichiometry in CuInSe$_2$ is explained here by the unusual stability of $(2V_{Cu}^0 + In_{Cu}^0)$. The lowest energy defect pair in ZnSe, i.e., $(V_{Zn}^0 + Se_{Zn}^0)$ requires $\sim$ 6 eV to form [16]. In contrast, In CuInSe$_2$ the formation of $(2V_{Cu}^0 + In_{Cu}^0)$ at the optimal chemical potential is exothermic $\Delta H = -1.46$ eV. Furthermore, there is a strong interaction between the components of the defect pairs which can lower the defect pair formation energy to as low as -6.1 eV/pair in a dense defect array. This low formation energy explains the existence of the previously unexplained unusual "Ordered Defect Compounds" (ODC) CuIn$_5$Se$_8$, CuIn$_3$Se$_5$, Cu$_2$In$_4$Se$_7$ and Cu$_3$In$_5$Se$_9$ as a repeat of a single $(2V_{Cu} + In_{Cu})$ unit for each n=4, 5, 7, 9 units, respectively of CuInSe$_2$.

(b) *The ability to dope CuInSe$_2$ via native defects:* The very efficient self-doping ability of CuInSe$_2$ is a consequence of the low formation energy of the Cu vacancy and its very shallow energy levels ($\sim$30 meV above the valence band maximum), as opposed to the *deeper* cation vacancy levels in II-VI compounds.

(c) *The electrically benign nature of the structural defects:* This is explained in terms of the electronic passivation of the In_{Cu}^{2+} deep level by V_{Cu}^-. We find that the $(2V_{Cu}^- + In_{Cu}^{2+})$ pair is electrically neutral, has no *deep* gap levels, and that the ordered defect compounds, e.g., CuIn$_5$Se$_8$, CuIn$_3$Se$_5$ and Cu$_3$In$_7$Se$_{12}$, all have larger band gaps (1.34, 1.26 and 1.21 eV, respectively) than CuInSe$_2$ (1.04 eV).

Similar calculations were performed for CuGaSe$_2$. Comparing to CuInSe$_2$, we find that it is more difficult to form $(2V_{Cu}^- + Ga_{Cu}^{2+})$ defect pairs in CuGaSe$_2$ than to from $(2V_{Cu}^- + In_{Cu}^{2+})$ defect pairs in CuInSe$_2$. Also, the Ga_{Cu} donor levels are much deep than the In_{Cu} donor levels, so off-stoichiometry and self passivation must be more limited in CuGaSe$_2$.

METHOD OF CALCULATION

We model the defect by placing it at a center of an artificially large unit cell containing N atoms of Cu/In/Se, and then we impose periodic boundary conditions on this "supercell". Now that the system is (artificially) periodic, we can solve its Schroedinger equation using band structure methods. The unphysical defect-defect interaction between adjacent supercells is reduced by increasing N systematically. The Schroedinger equation we solve includes interaction between all electrons (Column, exchange and correlation) as well as interactions between the electrons and the nuclei and interactions between the nuclei. The Schroedinger equation is solved self consistently. Atoms are displaced until the quantum-mechanical forces are zero. At this point, we compute the total energy $E(\alpha, q)$ for a cell containing defect α (vacancy, antisite, interstitial) in charge state q and $E(\text{CuInSe}_2)$ for the same supercell in the absence of the defect. We wish to distinguish between defect formation energy and defect transition energy:

The **defect formation energy** $\Delta H_f(\alpha, q)$ of defect α in charge state q depends on the Fermi energy ϵ_F as well as on the atomic chemical potentials μ [17]. In CuInSe$_2$, neglect Se-related defects,

$$\Delta H_f(\alpha, q) = \Delta E(\alpha, q) + n_{Cu}\, \mu_{Cu} + n_{In}\, \mu_{In} + q\, \epsilon_F, \tag{1}$$

where

$$\Delta E(\alpha, q) = E(\alpha, q) - E(\text{CuInSe}_2) \\ + n_{Cu}\, \mu_{Cu}^{solid} + n_{In}\, \mu_{In}^{solid} + q\, E_V, \tag{2}$$

$\epsilon_F = \epsilon_F^a - E_V$, $\mu_{Cu} = \mu_{Cu}^a - \mu_{Cu}^{solid}$ and $\mu_{In} = \mu_{In}^a - \mu_{In}^{solid}$ (a denotes absolute values). Here, the n's are the numbers of Cu, In atoms and q is the the number of electrons, transferred from the supercell to the reservoir in forming the defect cell.

There are some thermodynamic limits to (μ, ϵ_F): ϵ_F is bound between the valence band maximum E_V and the conduction band minimum E_C, and $\{\mu_{Cu}, \mu_{In}\}$ are bound by (i) the values that will cause precipitation of solid elemental Cu, In, and Se, so $\mu_{Cu} \le 0$ and $\mu_{In} \le 0$, (ii) by the values that maintain a stable CuInSe$_2$ compound, so $\mu_{Cu} + \mu_{In} + 2\mu_{Se} = \Delta H_f(\text{CuInSe}_2)$, where $\Delta H_f(\text{CuInSe}_2) = -2.0$ eV is the calculated formation energy of solid CuInSe$_2$ from the elemental solids, and (iii) by the values that will cause formation of binaries (e.g., Cu$_2$Se and In$_2$Se$_3$).

The **defect transition energy** level $\epsilon_\alpha(q/q')$ is the Fermi energy in Eq. (1) at which the formation energy $\Delta H_f(\alpha, q)$ of defect α of charge q is equal to that of defect α of another charge q', i.e.,

$$\epsilon_\alpha(q/q') = [\Delta E(\alpha, q) - \Delta E(\alpha, q')]/(q' - q). \tag{3}$$

For example, $\epsilon_\alpha(0/+)$ is a donor level and $\epsilon_\alpha(-/0)$ is an acceptor level, etc.

For CuInSe$_2$ we calculated $\Delta H_f(\alpha, q)$ for point defect $\alpha = V_{Cu}, V_{In}, In_{Cu}, Cu_{In}, Cu_i$ and selected defect pairs.
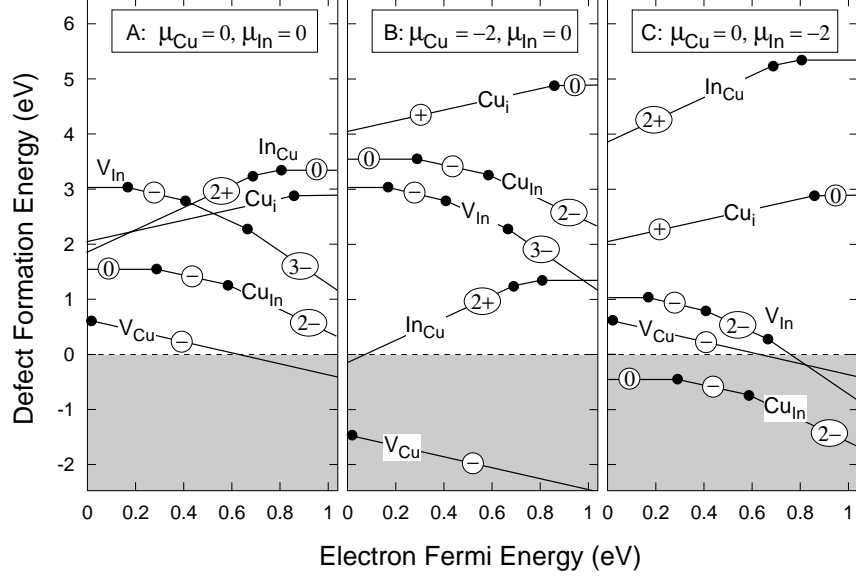
FIG. 1. Formation energies of $V_{Cu}, V_{In}, In_{Cu}, Cu_{In}$ and Cu_i, as a function of the electron Fermi energy ϵ_F (between the VBM and the CBM) at chemical potentials A, B and C. The shaded area highlights negative formation energies. Solid dots indicate "transition levels", where the charge state q of a defect changes.

The total energies and band structures are calculated using the local density functional formalism [18] as implemented by the general potential linearized augmented plane wave (LAPW) method [19]. The LDA error on the band gap is corrected by adding a constant potential to the conduction states so the band gap of CuInSe$_2$ matches the experimental value of 1.04 eV. We estimated that the uncertainty in our calculation of defect formation energy is ±0.2 eV per point defect. The uncertainty in point defect transition energy levels is estimated to be ±0.05 eV, and approximately ±0.1 eV for defect pairs. The uncertainty here comes mainly from the difficulty in determining the valence and conduction band edges in the defect-containing supercell.

DEFECT FORMATION ENERGIES

Table I lists the point defect formation energies $\Delta H_f(\alpha, q)$ in terms of $\Delta E(\alpha, q), n_{Cu}, n_{In}$ and q, as in Eq. (1). The Fermi energy dependence of the defect formation energy is shown in Fig. 1 at three limiting atomic chemical potentials: A($\mu_{Cu} = 0$, $\mu_{In} = 0$), B($\mu_{Cu} = -2$, $\mu_{In} = 0$), and C($\mu_{Cu} = -2$, $\mu_{In} = -2$). We see from Fig. 1 and Table I that:

(i) The relative stability of various defects depends critically on the chemical potentials: $\Delta H_f(V_{Cu})$ can vary by as much as 2 eV from point A to B, and $\Delta H_f(Cu_{In})$ can vary by as much as 4 eV from point B to C.

(ii) The formation energies also have a significant dependence on the Fermi energy. In general, acceptor states such as V_{Cu}^- form more easily in n-type material while donor states such as In_{Cu}^{2+} form more easily in p-type material.

(iii) Some of the formation energies of single neutral defects in CuInSe$_2$ are extraordinary low, e.g.,
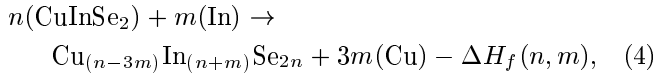
TABLE I. Defect formation energies $\Delta E(\alpha, q)$ of Eq. (2) and defect transition levels $\epsilon_\alpha(q/q')$ of Eq. (5). The n$_{Cu}$ and n$_{In}$ are the numbers of Cu and In atoms and q is the number of excess electrons, transferred from the defect-free crystal to the reservoirs to form one defect.

Defect α	$\Delta E(\alpha, q)$ (eV)		n$_{Cu}$	n$_{In}$	q
V_{Cu}^0	0.60		+1	0	0
V_{Cu}^-	0.63		+1	0	-1
Defect transition level:	(-/0)	$= E_V + 0.03$ eV			
V_{In}^0	3.04		0	+1	0
V_{In}^-	3.21		0	+1	-1
V_{In}^{2-}	3.62		0	+1	-2
V_{In}^{3-}	4.29		0	+1	-3
Defect transition levels:	(-/0)	$= E_V + 0.17$ eV			
	(2-/-)	$= E_V + 0.41$ eV			
	(3-/2-)	$= E_V + 0.67$ eV			
Cu_{In}^0	1.54		-1	+1	0
Cu_{In}^-	1.83		-1	+1	-1
Cu_{In}^{2-}	2.41		-1	+1	-2
Defect transition levels:	(-/0)	$= E_V + 0.29$ eV			
	(2-/-)	$= E_V + 0.58$ eV			
In_{Cu}^{2+}	1.85		+1	-1	+2
In_{Cu}^+	2.55		+1	-1	+1
In_{Cu}^0	3.34		+1	-1	0
Defect transition levels:	(0/+)	$= E_C - 0.25$ eV			
	(+/2+)	$= E_C - 0.34$ eV			
Cu_i^+	2.04		-1	0	+1
Cu_i^0	2.88		-1	0	0
Defect transition level:	(0/+)	$= E_C - 0.20$ eV			

$\Delta H_f(V_{Cu}^0) = -1.4$ eV (at B) and $\Delta H_f(Cu_{In}^0) = -0.5$ eV (at C). In particular, the formation energy of the Cu vacancy in CuInSe$_2$ is significantly lower than cation vacancy formation energies in II-VI's. There are two reasons for this: (a) low $E(\alpha, q) - E(CuInSe_2)$ and (b) large $|\mu_{Cu}^{solid}|$ in Eq. (2): (a) The low $E(\alpha, q) - E(CuInSe_2)$ has two contributions ("ionic" and "covalent"). The ionic reason is that Cu is monovalent, while cations in II-VI's are divalent, so the point-ion (Madelung) contribution to the removal energy of the cation is larger in II-VI's. The covalent reason is that the Cu-Se bond is easier to break than Zn-Se because the Cu 4p energy is higher than the Zn 4p energy (thus Cu-Se bond is less covalent). (b) The low μ_{Cu}^{solid} originates from the fact that solid Cu is more stable [20] ($\mu_{Cu}^{solid} = -E_{cohesive} = -3.49$ eV) than either solid In (-2.52 eV) or solid Zn (-1.35 eV) for V_{Zn} in ZnSe.

Figure 1 further reveals the coexistence of several low energy *point* defects in CuInSe$_2$. We find that it costs $\underline{\Delta H_{neutral} = 4.5}$ eV to form neutral non-interacting defect pairs $(2V_{Cu}^0 + In_{Cu}^0)$ The formation energy of this defect pair can be lowered considerably through interaction. The interaction includes (a) charge compensation, (b) subsequent Coulomb attraction and (c) atomic relaxations. We have analyzed the defects interaction energy δH_{int} for $(2V_{Cu}^- + In_{Cu}^{2+})$ defect pair. We find that in this case $\underline{\delta H_{int} = -4.2}$ eV of which (a) the transfer of two electrons from the high-energy donor level to low-energy acceptor level (i.e., charge compensation) releases ~ -1.4 eV, (b) a strong electrostatic attraction between the ensuing charged defects releases ~ -2.5 eV, and (c) atomic relaxations upon pairing releases -0.3 eV.

Defect pairs whose components are charged may further lower their formation energy at low temperature through ordering. The ordered arrays of the $(2V_{Cu}^- + In_{Cu}^{2+})$ defect pairs can be written as

$$n(CuInSe_2) + m(In) \rightarrow$$
$$Cu_{(n-3m)}In_{(n+m)}Se_{2n} + 3m(Cu) - \Delta H_f(n, m), \quad (4)$$

where m = 1, 2, 3, $\cdots$ and n = 3, 4, 5, $\cdots$, and where (In) and (Cu) denote In and Cu in their respective equilibrium chemical reservoirs. We find that the pair-pair ordering energy $\delta H_{ord}(n, m) = \Delta H_f(n, m) - \Delta H_f(2V_{Cu}^- + In_{Cu}^{2+})$ for the defect array $(2V_{Cu}^- + In_{Cu}^{2+})$ depends weakly on n. For m=1, it has an average value of $\underline{\delta H_{ord} = \sim -0.4}$ eV.

The analysis above show that the sum of the formation energy $\Delta H_{neutral} + \delta H_{int} + \delta H_{ord}$ for the defect pair array $(2V_{Cu}^- + In_{Cu}^{2+})$ is about -0.1 eV at point A. This formation energy of the defect array could be as low as -6.1 eV at point B. This low formation energy explains the existence of the previously unexplained unusual "ordered defect compounds" (ODC) CuIn$_5$Se$_8$, CuIn$_3$Se$_5$, Cu$_2$In$_4$Se$_7$ and Cu$_3$In$_5$Se$_9$ as a repeat of a single $(2V_{Cu} + In_{Cu})$ unit for each n=4, 5, 7, 9 units, respectively of CuInSe$_2$.

Similar results have been obtained for the formation energy of $(2V_{Cu}^- + Ga_{Cu}^{2+})$ in CuGaSe$_2$ (Table II). We find that at $\mu = \mu_{solid}$ (point A in Figure 1), it cost $\underline{\Delta H_{neutral} = 5.5}$ eV to form neutral $(2V_{Cu}^0 + Ga_{Cu}^0)$. The larger formation energy of the neutral defect pairs compared to that of $(2V_{Cu}^0 + In_{Cu}^0)$ (4.5 eV) in CuInSe$_2$ is due to the larger band gap of CuGaSe$_2$, thus larger formation energy of Ga_{Cu}^0. The interactions between $(2V_{Cu}^- + Ga_{Cu}^{2+})$ lower the formation energy by $\underline{\delta H_{int} = -4.8}$ eV. Defect pair ordering further lowers the formation energy of $(2V_{Cu}^- + Ga_{Cu}^{2+})$ array in CuGaSe$_2$ by $\underline{\delta H_{ord} = -0.5}$ eV. Thus, the total formation energy of $(2V_{Cu}^- + Ga_{Cu}^{2+})$ array in CuGaSe$_2$ is about 0.2 eV at point A. This results suggest that it is more difficult to form ordered defect compounds (ODC) in CuGaSe$_2$ than in CuInSe$_2$.

DEFECT TRANSITION ENERGY LEVELS

The solid dots in Fig. 1 denote points where the slope of $\Delta H_f(\alpha, q)$ vs q changes. The corresponding value of ϵ_F is the defect transition energy $\epsilon_\alpha(q/q')$ [Eq. (3)] listed in Table I. We see from Fig. 1 and Table I that the Cu vacancy has a shallow acceptor level $E(0/-) = E_V + 0.03$ eV, the In vacancy has a somewhat deeper level at $E(0/-) = E_V + 0.17$ eV. All other defect levels are relatively deep including the two In vacancy acceptor levels at 0.41 and 0.67 eV above E_V, respectively. The Cu_{In} antisite also has two deep acceptor levels at 0.29 and 0.58 eV above E_V. The deep donors in CuInSe$_2$ are the In_{Cu} antisite with two levels 0.25 and 0.34 eV below E_C, and the Cu interstitial with one level at 0.20 eV below E_C, respectively.
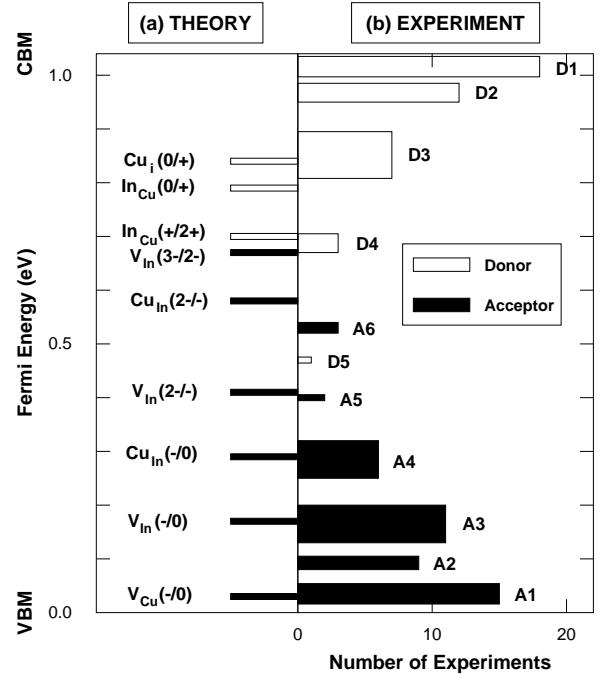

FIG. 2. Defect transition energy levels from (a) the current theory and (b) experiments. The filled histograms indicate acceptor levels while the open ones indicate donor levels. In (b), the horizontal axis indicates the number of experiments that have been performed and the widths of the histograms indicate the spread of the experimental data.
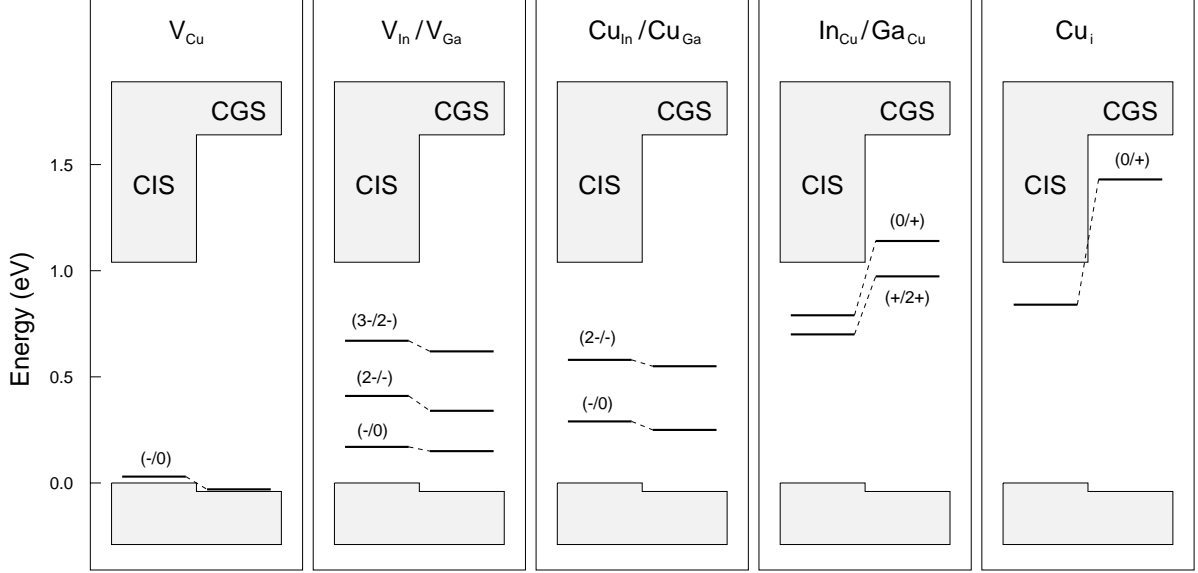
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FIG. 3. Comparison of defect energy levels in CuInSe$_2$ and CuGaSe$_2$. The acceptor levels (relative to the VBM) are similar in both material, but the donor levels (relative to the CBM) of Ga_{Cu} in CuGaSe$_2$ is much deep than the donor levels of In_{Cu} in CuInSe$_2$.

For isolated interacting $2V_{Cu}^- + In_{Cu}^{2+}$ pair, we find that the pairing pushes up the deep In_{Cu} levels to positions much closer to the conduction band minimum. So the In_{Cu} levels in the pair are no longer harmful electron traps. This, combined with the very low formation energy for this pair, explains the surprising electric tolerance of CuInSe$_2$ to large amount of structural defects. We also calculated the $(+/0)$ transition energy for $(In_{Cu} + V_{Cu})$ and find that it has a donor level located at $E_C - 0.20$ eV.

The calculated Cu vacancy level $E(0/-) = E_V + 0.03$ eV is considerably shallower than that of the double-acceptor $E(-/2-) = E_V + 0.47$ eV of the Zn-vacancy in ZnSe. (The measured $E(-/2-)$ level of the Zn-vacancy [21] is $E_V + 0.66$ eV. The difference between the calculated and measured values here may be accounted for by Jahn-Teller distortion not considered in the calculation.) Why is V_{Cu} in CuInSe$_2$ much shallower than V_{Zn} in ZnSe? The main reason is that in CuInSe$_2$ the VBM is pushed considerably higher by the repulsion between Cu 3d and Se 4p levels [22] than the VBM of ZnSe. Thus, the VBM of the CuInSe$_2$ is much closer to the defect level.

Fig. 2 compares our predicted defect transition levels (Fig. 2a) with experimental data (Fig. 2b) from various experimental techniques cited in Ref. 15b. The scattering of the experimental data is represented in Fig. 2b by the width of the histogram, whereas the height of the histogram indicates the number of experiments reporting that defect level. Comparing Fig. 2a and 2b, we see that: (i) Our calculated defect levels are in good accord with experiment, especially those of low ionizations, i.e., $(0/-)$ or $(+/0)$. Thus, the calculated $V_{Cu}(0/-)$ acceptor

level corresponds to the observed A1 level; the $V_{In}(0/-)$ level corresponds to the A3 level; the $Cu_{In}(0/-)$ level corresponds to the A4 level and the $V_{In}(2-/-)$ level corresponds to the A5 level. The $Cu_{In}(2-/-)$ level, within the uncertainty of the calculation, could be the A6 level. For donors, both the $Cu_i(+/0)$ and $In_{Cu}(+/0)$ levels may

TABLE II. Similar to Table I but for CuGaSe$_2$.

Defect α	$\Delta E(\alpha, q)$ (eV)		n$_{Cu}$	n$_{In}$	q
V_{Cu}^0	0.66		+1	0	0
V_{Cu}^-	0.67		+1	0	-1
Defect transition level:		$(-/0)$ = $E_V + 0.01$ eV			
V_{Ga}^0	2.83		0	+1	0
V_{Ga}^-	3.02		0	+1	-1
V_{Ga}^{2-}	3.40		0	+1	-2
V_{Ga}^{3-}	4.06		0	+1	-3
Defect transition levels:		$(-/0)$ = $E_V + 0.19$ eV			
		$(2-/-)$ = $E_V + 0.38$ eV			
		$(3-/2-)$ = $E_V + 0.66$ eV			
Cu_{Ga}^0	1.41		-1	+1	0
Cu_{Ga}^-	1.70		-1	+1	-1
Cu_{Ga}^{2-}	2.33		-1	+1	-2
Defect transition levels:		$(-/0)$ = $E_V + 0.29$ eV			
		$(2-/-)$ = $E_V + 0.61$ eV			
Ga_{Cu}^{2+}	2.04		+1	-1	+2
Ga_{Cu}^+	3.03		+1	-1	+1
Ga_{Cu}^0	4.22		+1	-1	0
Defect transition levels:		$(0/+)$ = $E_C - 0.49$ eV			
		$(+/2+)$ = $E_C - 0.69$ eV			
Cu_i^+	1.91		-1	0	+1
Cu_i^0	3.38		-1	0	0
Defect transition level:		$(0/+)$ = $E_C - 0.21$ eV			

be responsible for the measured D3 level which has a broad range of ~ 90 meV. The $In_{Cu}(2+/+)$ level corresponds to the D4 level. (ii) There are a number of misassignments of the defect levels in existing literature, including to assign (a) the A1 level to V_{In} [7]; (b) the A1 level to Cu_{In} [9]; (c) the D3 level to In_i [9]; and (d) the D1 level to both In_{Cu} [8,9] and Cu_i [8]. (iii) The shallow donor levels D1 and D2 are not resolved from the above calculations. However, it has been speculated that V_{Se} (which was not calculated here) is responsible for the D1 level. The D2 level, on the other hand, may be caused by the $(+/0)$ transition of the $(In_{Cu} + V_{Cu})$ pair or by $V_{Se}(2+/+)$. On the other hand, the unresolved A2 level could be the $(0/-)$ transition of the $(Cu_{In} + Cu_i)$ pair. The uncertainty ($\sim \pm 0.1$ eV) in the current calculation for defect pair energy levels makes it difficult to make a definitive assignment. (iv) The calculated $V_{In}(3-/2-)$ level is yet to be resolved experimentally. This level is featured by its deep position inside the band gap and a high ionization state (3-/2-).

Table II gives our calculated point defect transition energy levels for CuGaSe$_2$. The results are compared with the corresponding transition energy levels in CuInSe$_2$. We use our calculated band alignment [23] between CuGaSe$_2$ and CuInSe$_2$. We see that the acceptor levels in these two compounds are very similar. However, we find that the Ga_{Cu} donor levels is much deep than that of In_{Cu} donor levels. The reasons for this are two folds: (a) Ga is smaller than In, so lattice compression in CuGaSe$_2$ pushes up the CBM energy level of CuGaSe$_2$ (the CBM of CuGaSe$_2$ is 0.6 eV higher than CuInSe$_2$) and (b) the wavefunction of this antisite defect has s character and is localized on the group III atom. The Ga $4s$ orbital energy is about 0.7 eV lower than the In $5s$ orbital energy. This results indicate it will be more difficult to have n-type doping in CuGaSe$_2$ than in CuInSe$_2$.

CONCLUSION

We call for experimental testing of our predictions.

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